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Development of a novel magnetic monitoring system for Engineered Barriers of Geological Disposal Facilities

Nicola Rigonat

Thesis submitted for the degree of Doctor of Philosophy

School of GeoSciences
The University of Edinburgh
2017
“Science, my lad, is made up of mistakes, but they are mistakes which it is useful to make, because they lead little by little to the truth”

Jules Verne
Declaration

I composed this thesis, the work is my own. No part of this thesis has been submitted for any other degree or qualification.

Name          Nicola Rigonat          Date          27/02/2017
Acknowledgements

The present study was undertaken with funding from Radioactive Waste Management Limited (RWM) (http://www.nda.gov.uk/rwm), a wholly-owned subsidiary of the Nuclear Decommissioning Authority. RWM is committed to the open publication of such work in peer-reviewed literature, and welcomes e-feedback to rwmdfeedback@nda.gov.uk.

I would like to thank my supervisors Prof. Simon L. Harley and Dr. Ian B. Butler for their constant and precious support, either scientific or human, throughout all the phases of this PhD project. Many thanks to Dr. Adrian Muxworthy (Faculty of Engineering, Department of Earth Science & Engineering, Imperial College London) and Prof. Oliver Isnard (French National Centre for Scientific Research - Institut Néel - MRS, France · Grenoble, Rhône-Alpes) for the use of their research facilities.

I would like to make a special mention for all the people who gave me support and help during my research: Dr. Christian Mavris, Dr. Nicholas Odling, Dr. Jenny Tait and Prof. Wyn Williams.

Another relevant mention goes to all the members of the SAFE Barriers research group, and in particular to Dr. Simon Norris and Prof. Rebecca Lunn.

A special thanks to my “partners in crime” Rami, Axel, Carlos and Alice for having shared with me this long and productive period of my life.

Finally yet importantly, the most important thanks of all. This work is dedicated to my family and my fiancé Eva. This would have never been possible without your distant, but constant and unbreakable, love and support.
Abstract

The UK Committee on Radioactive Waste Management (CoRWM) recommended, in 2006, that geological disposal coupled with safe and secure interim storage should have been the way forward for the long-term management of the UK’s higher activity wastes. The design of the underground repository contemplates the presence of bentonite plugs to seal access galleries and deposition boreholes and hence the interaction between the clay-based backfill material and the underground water.

Remote monitoring of the fluid saturation of the barrier, the waste canisters and of the surrounding subsurface Geological Disposal Facility environment assumes a relevant importance to guarantee the safety of the repository and to increase the confidence and the reliance of the communities living in areas potentially affected by the repository over time.

This remote monitoring of the Engineered Barrier System represents a technical challenge due to the unsuitability of some of the traditional geotechnical techniques or to the intrinsic unreliability of many geophysical prospecting techniques in providing information about the evolution of the Thermo-Hydro-Mechanical-Chemical coupling of the system over long timescales up to and including post-closure evolution.

In this project, I offer an initial approach to an innovative way of using mineral magnetism, and, in particular, I analyse the possible exploitation of corrosion-induced variations of the magnetic properties of several magnetic materials to monitor water saturation in the Engineered Barrier System and its evolution through time.

Initially the reactivity of several natural and synthetic materials is tested under different “extreme” conditions to analyse the feasibility of the research concept and identify the materials more adapt to carry out the job. The effects that the corrosion of the magnetic materials has on the clay matrix is also analysed in detail throughout all the thesis work.

The initial tests lead to the identification of specific transitions in the hysteretic behaviour of three of the initial candidates (Nd-Fe-B, AlNiCo and SmCo alloys). These three materials are subsequently tested under conditions closer to a real
“evolved” Barrier System, where the groundwater interacts, with cementiferous grout producing hyperalkaline leachates.

The final tests consider the temporal evolution (after 4, 8 and 12 months) of the magnetic properties of these materials in a dysoxic environment under imposed fluid-flow.

The results show a clear change in the hysteretic properties of the three materials analysed and the feasibility of the monitoring of the Barrier fluid saturation in the short-term. Furthermore, the corrosion of the magnets, under the conditions applied, did not cause formation of non-swelling clays.
Lay summary
In the past 60 years the UK nuclear venture, civil and military, has left behind a conspicuous amount of radioactive material that needs to be safely stored in Deep Underground Geological Disposal Facilities. The main challenge that scientists and engineers are called to take is to guarantee the safety of the workers and of the environment around the disposal site for many generations to come (in the order of 100,000 years or more).

In the facility, the waste canister will be surrounded by a thick layer of clay, meant to protect it from corrosion and to protect the surrounding environment from radionuclides or heavy metals that could potentially migrate and contaminate underground resources such as potable water.

Hence, monitoring the stability of the barrier is a crucial point to guarantee the safety of the environment and increase the reliance of the communities interested by the facility. In the thesis I have explored the possibility of exploiting the corrosion-induced variations of the magnetic field of some permanent magnets to monitor water saturation of the clay barrier and eventual changes of water chemistry.

I have used several types of magnets commonly used in electronic appliances and even fridge magnets to determine the best candidate.

The results of the experiments clearly indicated that two magnets (NdFeB and SmCo) out of five initially listed showed clear variations of their magnetic properties, that will result in easily measurable changes in the magnetic field in an underground setting.

In addition, the corrosion of these Rare Earth magnets did not cause perturbation of the chemical, mineralogical and physical properties of the clay buffer, given that no corrosion-related, non-swelling neoformed clays were identified.
## Contents

1 Introduction ....................................................................................................................... 30
1.1 A short history of the British nuclear programme ....................................................... 30
1.2 Dealing with the residues of this nuclear venture ......................................................... 32
1.3 Geological Disposal of Nuclear Waste ........................................................................... 35
1.4 The Engineered Barrier System and the SAFE Barriers project ................................. 38
1.5 EBS remote monitoring ................................................................................................. 40
1.6 Magnetic Monitoring Materials (M³) project .............................................................. 42
1.7 Thesis outline ................................................................................................................. 44
2 Background: research on clays and magnetic materials .................................................. 46
2.1 Clays and Na-montmorillonite ....................................................................................... 47
  2.1.1 Alteration of Na-montmorillonite ............................................................................ 52
2.2 Permanent neodymium magnets .................................................................................. 60
  2.2.1 Nd-Fe-B alloys corrosion in humid or aqueous media ........................................... 64
2.3 Permanent SmCo magnets ........................................................................................... 68
  2.3.1 SmCo alloy corrosion in humid or aqueous media ................................................. 70
2.4 Permanent AlNiCo magnets ........................................................................................ 70
2.5 Permanent Ferrite magnets ......................................................................................... 71
2.6 Magnetite ..................................................................................................................... 72
3 Experimental and analytical methodologies .................................................................... 77
3.1 Experimental methodologies ....................................................................................... 77
  3.1.1 Preparation of clay ................................................................................................. 77
  3.1.2 Preparation of magnetite ....................................................................................... 77
  3.1.3 Preparation of synthetic magnets .......................................................................... 78
3.2 Preparation of samples for the batch experiments ......................................................... 78
  3.2.1 Magnetite/bentonite samples and control samples (BM series) ............................... 78
  3.2.2 Synthetic magnets/bentonite samples .................................................................... 80
3.3 Set-up of the long-term experiments in confined fluid flow regime ......................... 81
  3.3.1 Problems encountered during the confined-fluid flow experiments ...................... 88
3.4 Extraction of the samples ............................................................................................. 89
  3.4.1 Batch experiments ................................................................................................. 89
  3.4.2 Long-term experiments .......................................................................................... 90
3.5 Analytical methodologies ............................................................................................ 91
  3.5.1 XRPD analysis ....................................................................................................... 91
3.5.2 Magnetic analysis ................................................................. 96
3.5.3 ICP-OES analysis ................................................................. 98
3.5.4 Mössbauer analysis ............................................................... 98

4 Results of Batch Experiments ...................................................... 99

4.1 Introduction .............................................................................. 99
4.2 Batch Experiments – Nd-Fe-B Permanent magnets ...................... 100
  4.2.1 Summary and Discussion ..................................................... 115
4.3 Batch Experiments - SmCo permanent magnets ......................... 120
4.4 Batch Experiments - AlNiCo permanent magnets ....................... 125
4.5 Batch Experiments - Ferrite permanent magnets ......................... 129
4.6 Batch Experiments - Magnetite ................................................. 134
  4.6.1 Kirmag set – Control Samples .............................................. 136
  4.6.2 BMa Set – Five month-long experiment ................................. 137
  4.6.3 BMaW6b and BMβW6b Sets – Time-dependent experiment ...... 141
  4.6.4 Summary ............................................................................. 143
4.7 Batch Experiments – Clay Matrix Evolution ............................... 144
  4.7.1 MX80 sodium bentonite ....................................................... 145
  4.7.2 Control samples .................................................................... 147
  4.7.3 Magnetite/bentonite mixtures ............................................... 147
  4.7.4 Synthetic magnets/bentonite mixtures .................................... 152
  4.7.5 Summary of clay behavior ................................................... 162
4.8 Batch Experiments - Solution chemistry ...................................... 163
4.9 Batch Experiments - Concluding remarks .................................... 166

5 Results of Confined Fluid Experiments ......................................... 168

5.1 Introduction .............................................................................. 168
5.2 Confined Fluid Flow Experiments – Nd-Fe-B permanent magnets ........ 169
5.3 Confined Fluid Flow Experiments - SmCo permanent magnets ........ 178
5.4 Confined Fluid Flow Experiments - AlNiCo permanent magnets ........ 181
5.5 Confined Fluid Flow Experiments - Clay matrix ............................ 183
  5.5.1 Stack 2 – Control Sample (12 months) .................................. 184
  5.5.2 Stack 3A – 4 months ............................................................ 187
  5.5.3 Stack 3B – 8 months ............................................................ 193
  5.5.4 Stack 1 – 12 months ............................................................. 200
  5.5.5 Summary of clay behaviour .................................................. 206
5.6 Confined Fluid Flow Experiments – Concluding remarks .................. 207
6 Conclusions .......................................................................................... 213
7 Future developments ........................................................................... 214
8 Publications and conference posters .................................................. 219
Bibliography ............................................................................................ 220
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Air-Dried</td>
</tr>
<tr>
<td>AERE</td>
<td>Atomic Energy Research Establishment</td>
</tr>
<tr>
<td>AFm</td>
<td>Alumina, Ferric oxide, Monosulfate</td>
</tr>
<tr>
<td>AGM</td>
<td>Alternating Gradient Field Magnetometer</td>
</tr>
<tr>
<td>AGR</td>
<td>Advanced Gas Reactors</td>
</tr>
<tr>
<td>ANDRA</td>
<td>Agence Nationale pour la gestion des Déchets RadioActifs</td>
</tr>
<tr>
<td>BGI</td>
<td>Bayerisches GeoInstitut</td>
</tr>
<tr>
<td>BGS</td>
<td>British Geological Survey</td>
</tr>
<tr>
<td>C(A)SH</td>
<td>Calcium (Aluminium) Silicates Hydrate</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>CGN</td>
<td>China General Nuclear</td>
</tr>
<tr>
<td>CNNC</td>
<td>China National Nuclear Corporation</td>
</tr>
<tr>
<td>CoRWM</td>
<td>Committee on Radioactive Waste Management</td>
</tr>
<tr>
<td>CSH</td>
<td>Calcium Silicates Hydrate</td>
</tr>
<tr>
<td>DDL</td>
<td>Diffuse Double Layer</td>
</tr>
<tr>
<td>EBS</td>
<td>Engineered barrier System</td>
</tr>
<tr>
<td>EDF</td>
<td>Électricité De France</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene-Glycolated</td>
</tr>
<tr>
<td>ENRESA</td>
<td>Empresa Nacional de Residuos Radiactivos</td>
</tr>
<tr>
<td>EPSRC</td>
<td>Engineering and Physical Sciences Research Council</td>
</tr>
<tr>
<td>ESPRG</td>
<td>Earth Surface Processes Research Group</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated Ethylene Propylene</td>
</tr>
<tr>
<td>GDF</td>
<td>Geological Disposal Facility</td>
</tr>
<tr>
<td>GM</td>
<td>General Motors</td>
</tr>
<tr>
<td>HAW</td>
<td>High Activity Waste</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>HPFU</td>
<td>Hydrogens Per Unit Formula</td>
</tr>
<tr>
<td>HRL</td>
<td>Hard Rock Laboratory</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Emission Spectrometry</td>
</tr>
<tr>
<td>ID</td>
<td>Inner Diameter</td>
</tr>
<tr>
<td>IGD-TP</td>
<td>Implementing Geological Disposal – Technology Platform</td>
</tr>
<tr>
<td>ILW</td>
<td>Intermediate Level Waste</td>
</tr>
<tr>
<td>I/S</td>
<td>Illite/Smectite interstratifications</td>
</tr>
<tr>
<td>LLW</td>
<td>Low Level waste</td>
</tr>
<tr>
<td>MD</td>
<td>Multi-Domain</td>
</tr>
<tr>
<td>MRWS</td>
<td>Managing Radioactive Waste Safely</td>
</tr>
<tr>
<td>NAGRA</td>
<td>Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle</td>
</tr>
<tr>
<td>NDA</td>
<td>Nuclear Decommissioning Authority</td>
</tr>
<tr>
<td>NEA</td>
<td>Nuclear Energy Agency</td>
</tr>
<tr>
<td>NIB</td>
<td>Neodymium-Iron-Boron</td>
</tr>
</tbody>
</table>
NIRAS  Nationale Instelling voor Radioactief Afval en verrijkte Splijtstoffen
NIREX  Nuclear Industry Radioactive Waste Executive
NRVB  Nirex Reference Vault Backfill
OD  Outer Diameter
ONDRAF  Organisme National des Déchets Radioactifs et des matières Fissiles enrichies
OPC  Ordinary Portland Cement
PDF  Powder Diffraction File
PETG  Polyethylene terephthalate glycol
PSD  Pseudo-Single-Domain
PWR  Pressurized Water Reactor
RCF  Rock Characterization Facility
REE  Rare Earth Element
RH  Relative Humidity
RSA  Radioactive Substances Act
RWMD  Radioactive Waste Management Directorate
SAFE  Systems Approach For Engineered barriers
SD  Single Domain
SEM  Scanning Electron Microscope
SF  Spent Fuel
SKB  Svensk Kärnbränslehantering AB
SP  Superparamagnetic
SQUID  Superconducting Quantum Interference Device
THMC  Thermo-Hydro-Mechanical-Chemical
TMA  ThermoMagnetic Analysis
UK  United Kingdom
USA  United States of America
VSM  Vibrating Sample Magnetometer
WMO  Waste Management Organization
WP  Work Package
XRPD  X-Ray Powder Diffraction

Experiment names

NdB  NdFeB+bentonite
AlB  AlNiCo+bentonite
SmB  SmCo+bentonite
FeB  Ferrite+bentonite
Nd-only  NdFeB-only (NdFeB reacted without bentonite in solution only)
Al-only  AlNiCo-only (AlNiCo reacted without bentonite in solution only)
Sm-only  SmCo-only (SmCo reacted without bentonite in solution only)
Fe-only  Ferrite-only (Ferrite reacted without bentonite in solution only)
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na–montmorillonite</td>
<td>Na⁺⁰.⁰³³(Al₁.₅Fe³⁺₀.₂₃Mg²⁺₀.₂₇)(Al₀.⁰₆Si₃.₉₄)O₁₀(OH)₂</td>
</tr>
<tr>
<td>K–montmorillonite</td>
<td>K⁺⁰.⁴³(Al₁.₅Fe³⁺₀.₂₃Mg²⁺₀.₂₇)(Al₀.⁰₆Si₃.₉₄)O₁₀(OH)₂</td>
</tr>
<tr>
<td>Illite</td>
<td>K⁺⁰.₈(Al₁.₅Fe³⁺₀.₂₃Mg²⁺₀.₂₇)(Al₀.₅₃Si₃.₄₇)O₁₀(OH)₂</td>
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<tr>
<td>Muscovite</td>
<td>KAl₂(AlSi₃O₁₀)</td>
</tr>
<tr>
<td>Sanidine</td>
<td>KAlSi₃O₈</td>
</tr>
<tr>
<td>Calcite/Aragonite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Portlandite</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>Merlinite</td>
<td>(K, Ca, Na)₇Si₂₃Al₉O₆₄ * 23H₂O</td>
</tr>
<tr>
<td>Phillipsite</td>
<td>(Ca, Na₂, K₂)₃Al₆Si₁₀O₃₂ * 12H₂O</td>
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<tr>
<td>Clinoliptionite</td>
<td>(Na, K, Ca)₂₋₃Al₃(Al, Si)₂Si₁₃O₃₆ * 12H₂O</td>
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<td>Analcime</td>
<td>NaAlSi₂O₆·H₂O</td>
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<td>Heulandite</td>
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<tr>
<td>Hydrogrossular</td>
<td>Ca₃Al₂Si₂O₈(OH)₄</td>
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<tr>
<td>Quartz</td>
<td>SiO₂</td>
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<tr>
<td>Scolecite</td>
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<tr>
<td>Mesolite</td>
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<td>Natrolite</td>
<td>Na₂Al₂Si₃O₁₀ * 2H₂O</td>
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<td>Stilbite</td>
<td>NaCa₄(Si₂₇Al₉)O₇₂ * 28(H₂O)</td>
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<td>Fe–saponite</td>
<td>Ca₀.₂₅(Mg, Fe)₃((Si, Al)₄O₁₀)(OH)₂ * n(H₂O)</td>
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<tr>
<td>Vermiculite</td>
<td>(Mg, Fe⁺², Fe⁺³)₃<a href="OH">(Al, Si)₄O₁₀</a>₂ * 4H₂O</td>
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<tr>
<td>Berthierine</td>
<td>(Fe, Fe, Al, Mg)₂₋₃(Si, Al)₂O₅(OH)₄</td>
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<tr>
<td>Mineral</td>
<td>Formula/Composition</td>
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<td>------------------</td>
<td>---------------------------------------------------------</td>
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<tr>
<td>Chlorite</td>
<td>(Fe, Mg, Al)$_6$(Si, Al)$<em>4$O$</em>{10}$(OH)$_8$</td>
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<tr>
<td>NEO–magnet (φ–phase)</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
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<tr>
<td>NEO–magnet (ρ–phase)</td>
<td>Nd$_{1+x}$Fe$_4$B$_4$</td>
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<td>NEO–magnet (η–phase)</td>
<td>Nd$_3$Fe$_2$B$_6$</td>
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<tr>
<td>Magnetite</td>
<td>(Fe$^{3+}$)$_8$[(Fe$^{2+}$)$_8$(Fe$^{3+}$)$<em>8$]O$</em>{32}$</td>
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<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Maghemite</td>
<td>(8Fe$^{3+}$)$<em>A[40/3Fe^{3+} + 8/3\Delta]B_3$O$</em>{22}^{2-}$</td>
</tr>
<tr>
<td>Oxidised magnetite</td>
<td>Fe$<em>{2+1-x}^2$Fe$</em>{2+2x}^3$O$_{4+0.5x}$</td>
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<td>Goethite</td>
<td>α-FeOOH</td>
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<td>Lepidocrocite</td>
<td>γ-FeOOH</td>
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<td>Feroxyhyte</td>
<td>δ-FeOOH</td>
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<tr>
<td>Ferrihydrite</td>
<td>Fe$^{3+}$_2O$_3$ * 5H$_2$O</td>
</tr>
<tr>
<td>Albite</td>
<td>NaAlSi$_3$O$_8$</td>
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<td>Albite</td>
<td>CaCO$_3$</td>
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<td>Hydrocalumite</td>
<td>Ca$_4$Al$_2$O$_6$Cl$_2$ * 10H$_2$O</td>
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<tr>
<td>Mayenite</td>
<td>Ca$<em>{12}$Al$</em>{14}$O$_{33}$</td>
</tr>
<tr>
<td>Brucite</td>
<td>MgOOH</td>
</tr>
<tr>
<td>Boehmite</td>
<td>γ-AlO(OH)</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>Ca$_5$Si$<em>6$(O,OH)$</em>{18}$ * 5H$_2$O.</td>
</tr>
</tbody>
</table>
Figure 1-1: Representation of an aerial view of the surface facility (Copyright © NDA) 37

Figure 1-2: Schematic representation of the underground Geological Disposal Facility. (Copyright © NDA) 37

Figure 1-3: Schematic representation of the minimum and maximum depth of the underground GDF (left) and representation of the potential footprint of the underground GDF [15]. 38

Figure 1-4: Schematic figure of an EBS with highlighted the research subjects of the various work packages involved in this consortium. The pale blue oval highlights the work packages involved with the development of advanced remote monitoring techniques. 40

Figure 1-5: schematic representation of the fluid-rock interaction and solute diffusion in an EBS system, according to the French GDF concept (picture taken from [23]) 43

Figure 2-1: Montmorillonite 3D stick-and-ball crystal structure [35] 49

Figure 2-2: Expansion of the smectite structure as a function of water adsorption [42] 51

Figure 2-3: XRPD trace for NdFe$_3$B alloy [81]. 61

Figure 2-4: Nd-Fe-B magnets microstructure (Schultz et al. [86]) 62

Figure 2-5: Schematic illustration showing degradation of $\rho$-, $\eta$- and $\phi$-phase of Nd-Fe-B magnets in a hot and humid environment [86]. 65

Figure 2-6: XRPD traces of SmCo$_{7-x}$Zr$_x$ alloys with x = 0 – 0.8 [112] 69

Figure 2-7: Graphical approach using Mrs/Ms vs. Hcr/Hc with limits drawn after [129]. Day et al. fix the limits between Pseudo Single Domain and Multi Domain at 0.05 for Mrs/Ms and at 4 for Hcr/Hc [128]. Day et al. found that the calculated Single Domain critical size (transition to Multi Domain) for titanomagnetites depended on the compositional parameter x and on crystal elongation and varied between 0.08 and 0.26μm, but experimentally between 0.1 and 2μm. In general, titanomagnetite multi-domain grains are characterised by Mrs/Ms ≈ 0.05 and Hcr/Hc 5. The upper limit of the transitional Pseudo Single Domain area was fixed at Mrs/Ms = 0.5 after theoretical calculations. 76

Figure 3-1: Schematic representation of a cross-section of a reaction vessel and of a complete stack of reaction vessels (Stack 2, 3A or 3B). The black arrows indicate the direction of the advective flow, whereas the blue waves the diffusive flow within the bentonite. This design has the virtue of maintaining a buffered pH and total reactant concentrations. The bentonite matrix is intended as a low porosity buffer that minimizes the movement of metal ions in the system. The interaction between the vessels is minimal because any eventual dissolved material entering the advective system would be so diluted to have no effect on the stability or the chemistry of the following vessel. 83

Figure 3-2: In the left-hand side are the 2L-capacity water reservoirs with the grinded NRVB cement at the bottom. Gas tubing is red and water tubing transparent. Gas and water inlets are located within the grout layer whereas water outlet with the filtering system hangs at half the water column. The water tubing are connected to the reaction vessels stack through the black Norprene tubing which pass through the peristaltic pump. The bucket on the right-hand side of the picture was filled with cold water and served as cooling system for the outgoing water flow. 84

Figure 3-3: The stacks of the reaction vessels inside the oven (picture taken before the start of the experiment). Stack 2 is not visible, being behind stack 1. The heat exchange unit made of a big brass cylinder with the tubing coiled around is visible in the lower part of the picture. 85

Figure 3-4: Delrin® reaction vessel (1) on the top part of the picture with its lid (2) (and the two water tubing). On the bottom part the filtering system with the two smaller paper filers (3), the porous sintered glass disc (4) and the bigger paper filter (5). The paper filter was a Whatman No1 qualitative cellulose filter. 86

Figure 3-5: The vessels were filled with an initial layer of powdered bentonite, then the magnets were disposed in a sort of face-centred pentagonal fashion (in the picture, the vessel containing AlNiCo magnets is shown), then covered by another layer of bentonite. 87

Figure 3-6: Effects of the corrosion on the plastic lid by the Chlorine-rich solution. Between the outer walls and the lid step, the corrosion channels are visible. They reached a maximum length of 7-8 mm and a depth of 4 mm. 89
Figure 4-1: Picture of samples belonging to the NdFeB+bentonite set taken one month after the beginning of the experiment. From left to right samples reacted with deionized water, NaOH, KOH and Ca(OH)$_2$ solutions. In the first sample, the magnet has been pushed upwards (a) by the swelling bentonite matrix and there is presence of precipitated (b) orange-coloured material (Feroxyhydrate/Ferrihydrite?).

Figure 4-2: Picture of samples belonging to the NdFeB+bentonite set taken one month after the beginning of the experiment. From left to right samples reacted with KCl, NaCl, and CaCl$_2$ solutions. All three feature heavily oxidized magnetic particles, precipitation of orange-coloured (b) material (Feroxyhydrate/Ferrihydrite?) and partially swollen matrix (c). The water column, in all three samples, has a yellowish colour due to material in suspension or metals in solution (d).

Figure 4-3: Picture of samples belonging to the NdFeB+bentonite set taken two months after the beginning of the experiment. From left to right samples reacted with KCl, NaCl, and CaCl$_2$ solutions. Precipitation of black material (e) (goethite/lepidocrocite?) is present at the solution/bentonite interface and the haloes around the buried magnets are more visible than in Figure 4-2.

Figure 4-4: Picture of samples belonging to the NdFeB+bentonite set taken after the end of the experiment. From left to right samples reacted with NaCl, KCl, and CaCl$_2$ solutions. NaCl-solution treated sample features tensile fractures partially filled with solution and black coloured material. KCl- and CaCl$_2$-solution treated samples feature partially swollen matrix (c) and presence of black-coloured material precipitated at the solution/bentonite interface. The butyl septa appear all deformed and swollen for presence of hydrogen gas formed by the corrosion of the magnets.

Figure 4-5: XRPD traces of the Nd-Fe-B permanent magnets reacted with alkaline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. From bottom to top the raw material (black line), reacted with 0.1M NaOH solution (green line), reacted with 0.1M KOH solution (red line) and Ca(OH)$_2$ solution (blue line). Thick red (φ-phase) and violet (η-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples.

Figure 4-6: Hysteresis loops Nd-Fe-B permanent magnets reacted with alkaline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. The samples reacted within bentonite matrix (b) feature a transition from Pseudo Single Domain-like behaviour (red loop) to superparamagnetic material (green and blue loops). Loop of the raw material in Figure 5-4A.

Figure 4-7: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with alkaline solutions in aqueous media (left column) and within bentonite matrix (right column). These pie charts consider the main magnetic phases only. Passivated samples in NaOH and KOH solutions (left column) feature respectively 98 and 100 wt. % of raw Nd-Fe-B magnet, whereas the other samples a complex composition. The samples reacted within bentonite matrix show a clear predominance of NdFeB$_2$. The samples reacted with Ca-rich solutions all have a complex composition, with more hydrides present and in higher concentrations of each of the others.

Figure 4-8: (a) XRPD traces of the Nd-Fe-B permanent magnets reacted with deionized water in solution only. From bottom to the top raw Nd-Fe-B material (black line), then Nd-Fe-B reacted in water only (blue line) and Nd-Fe-B reacted within bentonite matrix (red line). Thick red (φ-phase) and violet (η-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples. (b) Hysteresis loops Nd-Fe-B permanent magnets reacted with aqueous media. Loop of the raw material in Figure 5-4A.

Figure 4-9: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with deionized water in aqueous media (left) and within bentonite matrix (right). This pie chart considers the main magnetic phases only. The sample reacted in bentonite matrix shows a relatively more homogeneous hydrogenation of the alloy, whereas the sample reacted in aqueous media a rather non-uniform hydrogenation with higher percentages of different hydrides.
Figure 4-10: XRPD traces of the Nd-Fe-B permanent magnets reacted with saline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. From bottom to the top raw material (black line), reacted with 1M NaCl solution (green line), reacted with 1M KCl solution (red line) and CaCl₂ solution (blue line). Thick red (φ-phase) and violet (η-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples.

Figure 4-11: Hysteresis loops Nd-Fe-B permanent magnets reacted with saline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. The samples reacted in solution only (a) show a very nice transition from Pseudo Single Domain-like loop (red and green loops) to a loop typical of a superparamagnetic material (blue), whereas the samples reacted within bentonite matrix (b) all feature loops of superparamagnetic materials. Loop of the raw material in Figure 5-A.

Figure 4-12: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with saline solutions in aqueous media (left column) and within bentonite matrix (right column). This pie chart considers the main magnetic phases only. All samples feature complicated compositions with most of the hydrogenated phases present in considerable amounts. Samples reacted in aqueous media on average have higher percentage of raw Nd-Fe-B phase and lower averaged hydrogen content.

Figure 4-13: HPFU vs. Curie temperature plot. The samples of the NdFeB-only (Nd-only) and NdFeB+bentonite (NdB) set are plotted with pure Nd-Fe-B hydrides [105]. The relative scatter of the samples from this study reflects their impure chemical compositions which causes shifts in temperature. Curie temperature error ±5°C, HPFU estimation error ±0.5.

Figure 4-14: HPFU vs. Coercivity plot. HPFU estimation error ±0.5.

Figure 4-15: Mrs/Ms vs. Hcr/Hc plot after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129]. The sample circled in blue is, considering the previous plots and figures (Figure 4-6 and Figure 4-14), a problematic point. From X-ray diffraction and Curie temperature data, the sample did not suffer high levels of corrosion and so should not fall in that area. The sample, during hysteresis analysis, was not saturated and hence its parameters are not correct. The boundaries between Single Domain, Pseudo Single Domain and Multi Domain areas are in dashed lines because they represent the limits given for mixtures of synthetic mixtures of magnetites and titanomagnetites with known grain sizes. The samples in this experiment do not have a known grain size and have very heterogeneous chemical and physical properties. The red box discriminates the cluster of samples reacted in deionized water and alkaline solutions, whereas the green box the samples reacted with saline or K-rich solutions.

Figure 4-16: Three examples of results of thermomagnetic analysis. Red curves represent the heating stage and the blue curves the cooling stage. (a) passivated Nd3-only; Curie temperature 311°C (b) corroded NdB7 sample; Curie temperature 376°C (c) corroded NdB3 sample; Curie temperature 376°C. The green circles highlight the areas of the heating curves generated by the presence of Fe oxyhydroxides or defected Fe oxides. All samples present a Curie point between 236-246°C. In the literature, Curie points in this area have been related to presence of defected iron oxides or defected iron oxides solid solutions. With the exception of the passivated sample, all other curves present an irreversible behaviour after heating, testifying the metastability of the Nd-Fe-B hydrides. The asterisks mark the presence of a rise to high susceptibility values called Hopkinson peak.

Figure 4-17: Abundance of Nd-Fe-B corrosion products in terms of total Fe oxides (magnetite, maghemite, hematite and iron α), total Fe oxyhydroxides (goethite, lepidocrocite, ferrihydrite and ferrithydrate) and Nd-rich phases (Nd(OH)₂, NdOH and NdH₂) in NdFeB-only (a) and NdFeB+bentonite (b) sets. The dashed lines represent the trend line of the respective mineral groups. y axis in in wt. %. Abundances were calculated from XRPD semi-quantitative data. Errors estimated ±1%.

Figure 4-18: Schematic illustration of a raw Nd-Fe-B alloy before corrosion (left) and as corrosion starts (right). The initial alloy is composed by ferromagnetic grains (φ-phase) with magnetic moment vectors all aligned in one direction. These grains and surrounded by a paramagnetic
interstitial phase (\(\rho\)-phase) that corrodes first causing the ferromagnetic grains to exfoliate. The exfoliation process leads the magnetic moment vectors to not be aligned anymore, causing the transition from a magnetocrystalline-single domain phase to a pseudo-single-domain phase. Blue arrows indicate the directions of the magnetic moment vectors.

Figure 4-19: Schematic representation of the corrosion process on an Nd\(_3\)Fe\(_{14}\)B (\(\varphi\)-phase) grain. The interstitial phase (\(\rho\)-phase) corrodes in accordance with Equation 4-1, and the corrosion-related phases precipitate at the grain boundary. The hydrogen produced at anode site is partially absorbed by the \(\varphi\)-phase to form layered Nd-Fe-B hydride complexes and partially diffuses as hydrogen gas.

Figure 4-20: Schematic representation of the formation of micro-crystals within the hydride layers around the core of unreacted Nd-Fe-B. Each micro-crystal has its own magnetic moment vector, not aligned with the magnetic vector of the raw Nd-Fe-B core.

Figure 4-21: From left to right samples of the SmCo+bentonite set reacted with 1M NaCl, 1M KCl and 1M CaCl\(_2\) solutions. Only the first sample features complete swelling of the matrix whereas the other two only a 200% swelling as observed in all the other experimental sets. One of the main characteristics is the presence of abundant quantities of red/orange precipitates at the solution/air interface and at the solution bentonite interface.

Figure 4-22: XRPD traces of SmCo permanent magnets reacted in aqueous solutions only (Sm only set). Intensity of the peaks reduced by two times for ease of display. y axis in counts/sec.

Figure 4-23: XRPD traces of SmCo permanent magnets reacted in bentonite matrix (SmCo+bentonite set). Intensity of the peaks reduced by two times for ease of display. y axis in counts/sec.

Figure 4-24: Hysteresis loops of the samples of the Sm only (A) and SmCo+bentonite set (B) reacted with deionised water. The black loop refers to the raw SmCo26 permanent magnet.

Figure 4-25: Hysteresis loops of the samples of the Sm only (A) and SmCo+bentonite set (B) reacted with alkaline solutions. The black loop refers to the raw SmCo26 permanent magnet, the green loops the samples reacted with 0.1M NaOH solution, the red loop the sample reacted with 0.1M KOH solutions and the blue loops the samples reacted with 0.05M Ca(OH)\(_2\) solutions.

Figure 4-26: Hysteresis loops of the samples of the Sm only (A) and SmCo+bentonite set (B) reacted with saline solutions. The black loop refers to the raw SmCo26 permanent magnet, the green loops the samples reacted with 1M NaCl solution, the red loop the sample reacted with 1M KCl solutions and the blue loops the samples reacted with 1M CaCl\(_2\) solutions.

Figure 4-27: From left to right, samples of the AlNiCo+bentonite set reacted with deionized water, 0.1M NaOH, 0.1M KOH and 0.05M Ca(OH)\(_2\) solution. The samples feature all complete swelling of the bentonite matrix, with formation of tensile fractures.

Figure 4-28: From left to right, samples of the AlNiCo+bentonite set reacted with 1M NaCl, 1M KCl and 1M CaCl\(_2\) solutions. Only the first sample features complete swelling of the matrix whereas the other two only a 200% swelling as observed in all the other experimental sets. One of the main characteristics is the presence of abundant quantities of red/orange precipitates at the solution/air interface and at the solution bentonite interface. The bentonite matrix presents an orange colour at the interface gently fading towards a yellow/pale-olive-green colour towards the untouched matrix.

Figure 4-29: Hysteresis loops of AlNiCo samples reacted in Na-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.

Figure 4-30: Hysteresis loops of AlNiCo samples reacted in K-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.

Figure 4-31: Hysteresis loops of AlNiCo samples reacted in Ca-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.

Figure 4-32: Mrs/Ms versus Hcr/Hc after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129]

Figure 4-33: (a) Sample FeBW5 (0.5M Ca(OH)\(_2\)) solution (b) Sample FeBW8 (1M CaCl\(_2\)) solution.

Figure 4-34: XRPD traces of Ferrites reacted in aqueous solutions only (Ferrite only set). Intensity of the peaks reduced by four times for ease of display. y axis in counts/sec.
Figure 4-35: XRPD traces of Ferrites reacted in bentonite matrix (Ferrite+bentonite set). Intensity of the peaks reduced by four times for ease of display. y axis in counts/sec.

Figure 4-36: Hysteresis loops of Ferrite samples reacted in Na-rich solutions. Ferrite-only set on the left, Ferrite+bentonite set on the right.

Figure 4-37: Hysteresis loops of Ferrite samples reacted in K-rich solutions. Ferrite-only set on the left, Ferrite+bentonite set on the right.

Figure 4-38: Hysteresis loops of Ferrite samples reacted in Ca-rich solutions. Ferrite-only set on the left, Ferrite+bentonite set on the right.

Figure 4-39: Mrs/Ms vs. Hcr/Hc plot after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129].

Figure 4-40: Fitted Mössbauer spectrum of sample Kirmag W8b (control sample not sieved reacted with 1M CaCl₂ solution).

Figure 4-41: Susceptibility curves for samples of the Kirmag set reacted in Na-rich solutions. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C.

Figure 4-42: Oxidation parameter (x) vs. Curie Temperature (T_C) diagram for the samples of Kirmag set. The red line represents the increasing Curie temperature of the magnetites.

Figure 4-43: Susceptibility curves for samples of the BMα set reacted in deionised water. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.

Figure 4-44: Susceptibility curves for samples of the BMα set reacted in 1M NaCl solution. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.

Figure 4-45: Susceptibility curves for samples of the BMα set reacted in 0.1M NaOH solution. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.

Figure 4-46: Oxidation parameter (x) vs. Curie temperature (T_C) diagram for samples of BMα set reacted with deionised water and alkaline solutions.

Figure 4-47: Susceptibility curves for samples of the BMαW6b and BMβW6b sets. The sample extracted after one month is on the left, whereas the one extracted after 5 months on the right. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. b: non-sieved magnetite.

Figure 4-48: Oxidation parameter (x) vs. Curie Temperature (T_C) diagram for samples of BMαW6b and BMβW6b sets.

Figure 4-49: Oriented mount of the air-dried clay fraction of the unreacted MX80 sodium bentonite supplied by RS minerals. The 001 reflection is centred at 12.5 Å and does not present pronounced shoulders.

Figure 4-50: Random mount of the accessory minerals fraction of the unreacted MX80 sodium bentonite supplied by RS minerals. (Ms = muscovite, Qz = quartz, Ab = albite, Sa = sanidine, Cal = calcite).

Figure 4-51: XRPD traces of oriented mounts of MX80 sodium bentonite after glycol-solvation and heating at 400 and 550°C.

Figure 4-52: XRPD traces of MX80 Na-montmorillonite control samples. Samples reacted with Ca-rich solutions feature AD 001 peak shifted towards lower angles whereas K-rich solutions caused a shift towards higher angles. Samples treated with saline solutions show higher levels of noise. For the composition of W6, refer to Table 3.2.

Figure 4-53: XRPD traces of clay matrix of samples of BMb/α-β set (reacted with W6).
Figure 4-54: XRPD traces of air-dried, glycol-solvated, 400° and 550°C heated clay specimens from set BMcu. Lines with the same colour belong to the same sample. For the composition of W6, refer to Table 3.2.

Figure 4-55: XRPD traces of air-dried and glycol-solvated clay specimens from Ferrite+bentonite set. Lines with the same colour belong to the same specimen.

Figure 4-56: XRPD traces of 400°C and 550°C heated clay specimens from Ferrite+bentonite set. Lines with the same colour belong to the same specimen.

Figure 4-57: XRPD traces of air-dried, glycol-solvated, 400° and 550°C heated clay specimens from set AlNiCo+bentonite. Lines with the same colour belong to the same specimen.

Figure 4-58: XRPD traces of air-dried and glycol-solvated clay specimens from SmCo+bentonite set. Lines with the same colour belong to the same specimen.

Figure 4-59: XRPD traces of 400°C and 550°C heated clay specimens from SmCo+bentonite set. Lines with the same colour belong to the same specimen.

Figure 4-60: XRPD traces of air-dried and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures.

Figure 4-61: XRPD traces of air-dry and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures and sampled at the magnet/matrix interface. The traces were all smoothed and the background removed. All the 001 reflections result very small and broad peaks (Air-dried KCl-solution trace is flat) that slightly increase in intensity and shift towards lower diffraction angles after glycol-solvation.

Figure 4-62: XRPD traces of air-dry and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures and sampled in the unaltered matrix. The positions of 001 reflections in the air-dry traces of KCl- and NaCl-solution treated samples show significant deviation from the CaCl2-water treated sample but they all centered at 16.8Å after glycol-solvation.

Figure 4-63: Metal ions in solution in bentonite porewater in the samples of NdFeB+bentonite set.

Figure 4-64: Metal ions in solution in bentonite porewater in the samples of AlNiCo+bentonite set.

Figure 4-65: Metal ions in solution in bentonite porewater in the samples of SmCo+bentonite set.

Figure 4-66: Metal ions in solution in bentonite porewater in the samples of Ferrite+bentonite set.

Figure 5-1: XRPD traces of the coated Nd-Fe-B magnets extracted from Stacks 3A, 3B and 1 (from bottom to top) compared with the raw Nd-Fe-B alloy. Peaks of the main magnetic phase in the corroded magnets are slightly shifted towards lower diffraction angles (red dashed lines).

Figure 5-2: XRPD traces of the uncoated Nd-Fe-B magnets extracted from stacks 3A, 3B and 1 (from bottom to top) compared with the raw Nd-Fe-B alloy. Peaks of the main magnetic phase in the corroded magnets are shifted towards lower diffraction angles (red dashed lines).

Figure 5-3: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the uncoated Nd-Fe-B magnets (left column) and of the coated Nd-Fe-B magnets (right column). These pie charts consider the main magnetic phases only.

Figure 5-4: Hysteresis loop of the raw Nd-Fe-B magnet (A) and of the coated Nd-Fe-B magnets extracted after 4 months (B), 8 months (C) and 12 months (D). The red dashed lines in (B) and (D) represent the magnetization curve.

Figure 5-5: Hysteresis loop of the raw Nd-Fe-B magnet (A) and of the uncoated Nd-Fe-B magnets extracted after 4 months (B), 8 months (C) and 12 months (D). The red dashed lines in (B), (C) and (D) represent the magnetization curve.

Figure 5-6: Thermomagnetic curves of the raw N42 Nd-Fe-B permanent magnet (A) and of the coated Nd-Fe-B magnets extracted after 4 (B), 8 (C) and 12 months (D). The black lines indicate Curie points of the magnetic phases.

Figure 5-7: Thermomagnetic curves of the raw N42 Nd-Fe-B permanent magnet (A) and of the uncoated Nd-Fe-B magnets extracted after 8 (B) months. The black lines indicate Curie points of the magnetic phases.

Figure 5-8: Hysteresis loops of the unreacted SmCo magnet (A) and of the SmCo magnets reacted for 4 (B), 5 (aborted sample, C) and 12 months (D). Green circles show areas where the hysteresis loop shows some steps due to presence of “soft” magnetic phases, and the red circle an indentation of the hysteresis loop marking the presence of a secondary “hard” magnetic phase.
Figure 5-9: Thermomagnetic curves of the SmCo permanent magnets extracted after 4 (B), 5 (C) and 12 months (D) and of the initial SmCo26 permanent magnet (A). Vertical axes represent the signal percentage in comparison to the magnetization saturation of the sample.

Figure 5-10: Hysteresis loops of the unreacted AlNiCo magnet (A) and of the AlNiCo magnets reacted for 4 (B), 8 (C) and 12 months (D). The red dashed lines represent the magnetization curve.

Figure 5-11: Thermomagnetic curves of the AlNiCo permanent magnets extracted after 4 (B), 8 (C) and 12 months (D) and of the initial AlNiCo permanent magnet (A). Vertical axes represent the signal percentage in comparison to the magnetization saturation of the sample. Increasing magnetization of the cooling curves is explained by stress relaxation post-heating.

Figure 5-12: Air-dried and glycol-solvated samples from the “soft” (A) and “encrusted” (B) areas of the control bentonite vessel of stack 2.

Figure 5-13: 400°C and 550°C heated samples from the “soft” (A) and “encrusted” (B) areas of the control bentonite vessel of stack 2.

Figure 5-14: XRPD traces of coarse accessory phases in the “encrusted” and “soft” areas of the control bentonite vessel.

Figure 5-15: XRPD traces of random mounts of samples from the “encrusted” and “soft areas of the control bentonite vessel.

Figure 5-16: Post-extraction photograph of uncoated Nd-Fe-B + bentonite sample. The cylinder is 5 cm in diameter and 1 cm in height. The sample is shown upside-down but the thin “encrusted” layer is visible at the bottom. Two patches of orange-coloured precipitates are visible and may be caused by precipitation of Fe oxyhydroxides or, more likely, by precipitation of plastic corrosion-related phases.

Figure 5-17: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-18: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “encrusted” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-19: 400°C- and 550°C-heated clay fraction of samples from the “encrusted” and “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference. The traces of the “encrusted” areas of SmCo and AlNiCo samples are not shown because the basal reflection had been destroyed upon heating.

Figure 5-20: XRPD traces of coarse accessory phases in the “encrusted” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

Figure 5-21: XRPD traces of coarse accessory phases in the “soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

Figure 5-22: XRPD traces of random mounts of samples from the “encrusted” areas.

Figure 5-23: XRPD traces of random mounts of samples from the “soft” areas.

Figure 5-24: Post freeze-drying picture of the “Soft” clay area still encasing the corroded magnet (A) and post-extraction picture of the “encrusted” clay (B) of the matrix of the uncoated Nd-Fe-B/bentonite vessel. The tip of the scalpel is shown as size reference.

Figure 5-25: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-26: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “encrusted” areas of bentonite matrix. The peaks relative d-spacing are shown as reference. The asterisk indicates the broad left shoulder in the area 5.6-6.1°2θ.

Figure 5-27: 400°C- and 550°C-heated clay fraction of samples from the “encrusted” and “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-28: XRPD traces of coarse accessory phases in the “encrusted” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

Figure 5-29: XRPD traces of coarse accessory phases in the “soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

Figure 5-30: XRPD traces of random mounts of samples from the “encrusted” areas.

Figure 5-31: XRPD traces of random mounts of samples from the “soft” areas.
Figure 5-32: Close-up photograph of the “encrusted” clay material sampled in the coated Nd-Fe-B vessel. In the red circle, the layered material is visible.

Figure 5-33: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-34: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “encrusted” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-35: 400°C- and 550°C-heated clay fraction of samples from the “encrusted” and “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

Figure 5-36: XRPD traces of coarse accessory phases in the “Encrusted” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

Figure 5-37: XRPD traces of coarse accessory phases in the “Soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display. The asterisk marks 2M1 muscovite or Illite.

Figure 5-38: XRPD traces of random mounts of samples from the “encrusted” areas. The asterisk marks a sharp reflection belonging to calcium aluminium oxide phase.

Figure 5-39: XRPD traces of random mounts of samples from the “soft” areas.

Figure 7-1: The essence of the MMM concept. Yellow segments form the bentonite buffer ring/sleeve in the HLW EBS. Orange arrows join the parts of this from the larger scale (full-segmented sleeve, 1.5-metre radius) to single bentonite segment both without and with embedded magnets (Neomagnets in this example). The blue disc is a magnified view of a single axially magnetised N42 Nd-Fe-B.
List of Tables

Table 2-1: Summary of the results of experimental and modelling works on bentonite/cement interaction relevant to this thesis.

Table 2-2: Summary of the results of experimental and modelling works on bentonite/iron interaction relevant to this thesis.

Table 3-1: Synthetic magnets used in the long-term experiments. The differences in the dimensions are due to the availability of stocks and the impossibility of obtaining custom made magnets in small lots.

Table 3-2: Composition of the solutions used in the batch experiments with pH values.

Table 3-3: List of samples of the batch experiments using magnetite. In blue are presented the control samples (magnetite only) and in green the samples of the bentonite-magnetite mixtures. a: magnetite powder (<10 μm), b: bulk crushed magnetite, c: grain size > 120 μm. W1-8 refers to solution composition in Table 3-2. MT magnetite-only, BM bentonite/magnetite

Table 3-4: List of the samples of batch experiments using the synthetic magnets embedded in bentonite (NdFeB+bentonite, AlNiCo+bentonite, SmCo+bentonite and Ferrite+bentonite sets).

Table 3-5: List of the synthetic magnets control samples of batch experiments (NdFeB-only, AlNiCo-only, SmCo-only and Ferrite-only sets). W1-8 refers to solution composition in Table 3-2.

Table 3-6: List of stacks used in the long-term experiments.

Table 3-7: Results of the Semi-quantitative XRPD analysis on the sample Coated Nd-Fe-B from Stack 1 of the Confined-Fluid-Flow experiments. The error calculated by DIFFRAC.TOPAS for the Nd-Fe-B hydrides ranges from ±0.8 to ±1.3.

Table 4-1: Curie temperatures, Sextet ratio (R) and oxidation parameter (x) for the magnetites of the Kirmag set. All the samples result being either weakly or moderately oxidised magnetites. For the composition of the mixed solution refer to W6 in Table 3.2.

Table 4-2: Curie temperatures, Sextet ratio (R) and oxidation parameter (x) for the magnetites of the BMu set reacted with deionised water and alkaline solutions. All the samples result being either weakly or moderately oxidised magnetites.

Table 4-3: Curie temperatures, Sextet ratio (R) and oxidation parameter (x) for the magnetites of the BMu set reacted with saline solutions. All the experiments yield weakly oxidised magnetites. Magnetic analysis on samples BMuW8a and BMuW8b were affected by a non-resolvable technical problem so this measurement was aborted. Sample BMuW2c presented a negative oxidation parameter due to excessive error during the spectroscopic analysis.

Table 4-4: Curie temperatures, Sextet ratio (R) and oxidation parameter (x) for the magnetites of the BMu set reacted with deionised water and alkaline solutions. Samples show different degrees of oxidation. For the composition of the mixed solution, refer to W6 in Table 3.2.

Table 5-1: Composition and magnetic properties of magnets and relative encasing matrix extracted from Stack 3A. Within square brackets, the values of the magnetic properties of the raw materials are presented for comparison.

Table 5-2: Composition and magnetic properties of magnets and relative encasing matrix extracted from Stack 3B. Within square brackets, the values of the magnetic properties of the raw materials are presented for comparison. The SmCo vessel was extracted after 5 months due to failure of the vessel.

Table 5-3: Composition and magnetic properties of magnets and relative encasing matrix extracted from Stack 3A. Within square brackets, the values of the magnetic properties of the raw materials are presented for comparison.
Definitions of commonly used acronyms or abbreviations

- **Coercive Force** (Hc): Field required to move pinned domain walls or rotate single-domain magnetization [1].
- **Curie Temperature** (Tc): Ordered magnetic moments (ferromagnetic) change and become disordered (paramagnetic) above the Curie temperature. Spontaneous magnetization occurs only below Tc.
- **Domain**: Region of a crystal where the magnetization is uniform and equal to the saturation magnetization.
- **Hard magnetic phase**: Magnetic phase with high coercivity
- **Hopkinson Peak Effect**: If the temperature is increased, the relaxation time decreases, particularly just below the Curie temperature, where the saturation magnetization drops to zero. In these conditions, the magnetization vectors of individual Single Domain grains reorient themselves in response to an applied field H, and this causes the susceptibility to rise to high levels (in case of superparamagnetic materials), forming a Hopkinson peak [1]. Domain wall mobility and ease of domain rotation increase with increasing temperature but because of strong self-demagnetizing effect in Multi Domain grains there is only a small increase in susceptibility, creating a low Hopkinson peak [1].
- **Hysteresis**: The hysteresis is a loop obtained by applying to a magnetic specimen a cyclic external magnetic field H and recording the change of the magnetization M or the magnetic induction B along the field direction.
- **Magnetocrystalline anisotropy**: energy necessary to deflect the magnetic moment in a single crystal from the easy to the hard direction
- **Maximum Energy Product**: is a measurement for the maximum amount of magnetic energy stored in a magnet. It concerns the product maximally attainable with a material made out of flux density B and field strength H.
- **Multi-Domain** (MD): Containing more than one magnetic domain. Magnetization changes occur mainly by moving walls or nucleating or denucleating domains [1].
- **Pseudo-Single Domain** (PSD): A remanence or magnetization structure, which is either non-uniform or occurs in grains larger than the equilibrium
Single Domain size. It still has some parameters typical of single-domain materials, like high coercive force and saturation remanence.

- **Remanent Coercivity or Coercivity of Remanence** (Hcr): Field-axis intercept of the remanent hysteresis loop.
- **Remanent magnetization or Remanence** (Mrs): Net magnetization remaining in zero applied field [1].
- **Saturation Remanence** (Ms): Remanence remaining after removal of a field large enough to saturate the induced magnetization [1].
- **Single-Domain** (SD): Crystal containing only one domain. Magnetization changes occur rotating all, or most, atomic spins at the same time.
- **Soft Magnetic phase**: Magnetic phase with low coercivity
- **Superparamagnetic** (SP): A condition in which magnetization changes are thermally activated in times much shorter than observation times, usually at high temperatures or small grain sizes. An ensemble of such grains has an equilibrium magnetization [1].
1 Introduction
In the last decades, with the decommissioning of the oldest power stations and the continuously increasing volumes of irradiated materials, governments around the world and the public have become increasingly concerned about the safe disposal of the nuclear wastes produced by over 60 years of nuclear power generation. The recent turmoil in many countries in the Middle East and the acts of terrorism in Europe, as well as the tragic accidents like Chernobyl in 1986 and Fukushima in 2011 have highlighted the necessity to develop safe and secure waste disposal frameworks, in order to guarantee the safety of the communities as well as gain positive public opinion about the absolute security of the reprocessing, interim storage or underground repository facilities. Hence, there is a need of establishing a well-detailed safety case for the disposal of the produced wastes.

This PhD project, part-funded by the Nuclear Decommissioning Authority (NDA) through the EPSRC (Engineering and Physical Sciences Research Council) is aimed at contributing to the foundations underpinning the safety case for a UK Disposal Facility. Despite being funded by NDA, the findings of this project might be beneficial to all countries that are developing or will develop plans for deep underground storage of nuclear wastes.

The purpose of this research is to investigate the possibility of remote, safe and non-invasive monitoring of groundwater ingress and chemical variation within the Engineered Barrier System (EBS) of a conceptual High Level Waste (HLW) repository within a Geological Disposal Facility (GDF). This work addresses a novel approach to monitoring of groundwater ingress and represents a feasibility study of the first principles of it.

Before explaining this project further, it is useful to take a step back and examine the nuclear history of the UK and the milestones of waste management in the last 30 years.

1.1 A short history of the British nuclear programme
The British nuclear history started in 1947, when the UK’s first nuclear reactor was built at the Atomic Energy Research Establishment (AERE). It was consolidated between 1954 and 1955 following the decision to carry out nuclear research for the purposes developing nuclear weapons for the army and reactors for commercial use.
The United Kingdom was the first country to establish a civil nuclear program after opening Calder Hall, the first nuclear power station in the world, in 1956. Since then, the nuclear program has further expanded, reaching its peak in 1997, when 26% of the total electricity produced was generated from nuclear stations. Since that time, the production of electricity from nuclear has progressively declined, to 19% by 2012 [2] mainly due to the decommissioning of the oldest Magnox power stations (Wylfa Nuclear is the last of its kind and is due to be closed by 2017-18).

At present nine power stations are active in the United Kingdom. One is an old Magnox type (Wylfa), seven are Advanced Gas-Cooled Reactors (AGR) type stations (Dungeness B, Hartlepool, Heysham1 and 2, Hinkley Point B, Hunterston B and Torness) and one is a Pressurized Water Reactor (PWR) station (Sizewell B). A further ten have been closed and entered decommissioning in the period between 1989 and 2012. Eight of the nine currently active nuclear power stations are due to close for decommissioning by 2023.

The UK energy plan for the future includes the construction of new, safer and more advanced power stations with the clear aim to reduce the nation’s carbon footprint and diminish the dependence from fossil fuel. The principal condition on the project is that no public money is to be used to build the new plants, and so all the economic cost will be sustained by developers (mainly EDF and Centrica, which bought the company previously operating the British nuclear stations in an 80/20 share).

There are proposals for building new plants at Hinkley Point C and Sizewell C (from EDF energy, Areva, CGN and CNNC), Wylfa and Oldbury (from Horizon Nuclear and Hitachi-GE) and Moorside (from NuGeneration) and Bradwell (from CGN). The works are proposed to start no later than 2020 [3].

Along with its civil nuclear program, the UK established one of the biggest military nuclear programs, which currently accounts for 160 operationally available warheads out of 250 declared warheads [4]. Furthermore, the UK also has had one of the world’s most advanced nuclear reprocessing plants (Sellafield, Cumbria) which incorporates two reactors undergoing dismantling and decommissioning.
1.2 Dealing with the residues of this nuclear venture
These nuclear programs have left behind a considerable amount of contaminated waste and spent fuel that have to be disposed safely within the territory of the owner’s country. This project’s co-funder, the Nuclear Decommissioning Authority (NDA) is tasked with the cleaning up of the UK’s nuclear legacy, and the quest for a suitable location for the future Geological Disposal Facility (GDF) of the nuclear waste produced in this country, a task devolved to RWM Ltd.

The first steps towards the study and the implementation of the deep geological disposal of radioactive waste were made in 1982 with the establishment of the Nuclear Industry Radioactive Waste Executive (NIREX).

In 1991, Nirex announced plans to build a rock characterisation facility (RCF) at a site near Sellafield but this was rejected by Cumbria County Council. An appeal by Nirex led to a public inquiry in 1995-96 but, shortly before a general election in March 1997, the then Secretary of State for the Environment, John Gummer, rejected the application [3] [5]. In 1997, two nuclear waste stores were built at Sellafield, with the plan of building ten more in the future.

The UK government Managing Radioactive Waste Safely (MRWS) programme was launched in 2001 [5] and its main scope was, and still is, to find a safe and practicable solution for the UK’s higher activity waste. The program has, as its main purpose, the long-term protection of people and environment, to work in an open and transparent way with a solid basis in sound science and the assurance of the effective use of public monies [6].

In 2002, as part of the MRWS programme, the government established an independent Committee on Radioactive Waste Management (CoRWM) [5]. CoRWM considered all options for managing radioactive waste using the available scientific knowledge and engaging and interested parties in the process [5]. CoRWM published the “Long List of Options” in 2004 and finally made its recommendations to Government in July 2006. UK government accepted CoRWM’s principal recommendation that geological disposal coupled with safe and secure interim storage should be the way forward for the long-term management of the UK’s higher activity wastes in October 2006 [5].

The Nuclear Decommissioning Authority (NDA) was established as a non-departmental public body of the United Kingdom by the Energy Act 2004 and started operating in 2005. In 2007, it set up the Radioactive Waste Management Directorate
(RWMD), now RWM Ltd., which has the responsibility for the geological disposal facility programme.

On the 25\textsuperscript{th} of June 2007, the UK government, together with the administrations of Wales and Northern Ireland, published a MRWS consultation paper covering the technical aspects of design and delivery of a geological disposal facility as well as the process and the criteria to be used for the siting of the facility [6]. The results of the consultation were analysed and reported in January 2008 and taken into account in the development of the “MRWS White Paper” published in 2008 [6].

Once the government established that deep geological disposal of higher activity nuclear waste (preceded by robust interim near-surface storage) was the way forward, the policy on the subject of nuclear waste disposal included several additional aspects. One of the most important is the participation of the local communities in the decision on the most suitable location for the Geological Disposal Facility. The UK policy is based on voluntarism and partnership with local communities.

The MRWS 2008 White Paper divided the Higher Activity Wastes (HAW) in the following categories, following the Radioactive Substances Act 1993 (or RSA93):

- **High Level Waste (HLW):** “wastes in which the temperature may rise significantly due to their radioactivity, so that this has to be taken into account in designing storage or disposal facilities”. The material is vitrified in borosilicate glass and poured into 150 litres capacity stainless steel containers, which are stored for at least 50 years near the surface to allow a significant proportion of the radioactivity to decay [6].

- **Intermediate Level Waste (ILW):** “wastes with radioactivity levels exceeding the upper boundaries of Low Level Waste, but which do not require heating to be taken into account in designing storage or disposal facilities”. The material is packaged, for example, by encapsulation in cement in 500 litre stainless steel drums [6].

Higher Activity Wastes also contain a small fraction of the so-called Low Level Waste (LLW), which are defined as: “Radioactive wastes having a radioactive content not exceeding 4 GBq/te of alpha or 12 GBq/te of beta/gamma activity” [7]. These make up 90\% of the volume of UK’s nuclear waste but contain less than 0.1\% of the
radioactivity and hence do not require deep geological disposal unless containing a significant concentration of specific radionuclides” [6].

Other radioactive materials, not currently classified as wastes, are:

- Spent Fuel (SF): Fuel used in nuclear power stations from MAGNOX was reprocessed giving reusable Uranium and Plutonium and HLW, ILW and LLW to be disposed. SF from AGR and PWR does not need reprocessing and hence can be disposed immediately.

- Plutonium and Uranium

As 2007, the Radioactive Waste and Materials inventory consisted of 476,900 m³ of materials with ILW accounting for 76% of the volume and 2.5% of the radioactivity, SF for 2.3% of the volume and 51.6% of the radioactivity and HLW for 0.3% of the volume and 41.3% of the radioactivity (radioactivity calculated at 2040).

The government’s framework for the implementation of the Geological Disposal was further set out with the “Implementing Geological Disposal White Paper” published in 2014, which also defined the waste inventory in terms of the types of waste and nuclear materials that may be designated as waste in the future [8].

According to the Implementing Geological Disposal White Paper, the specific types of waste and nuclear materials are the following:

- HLW arising from the reprocessing of spent fuel at Sellafield
- ILW arising from existing licensed nuclear sites and defence, medical, industrial and educational activities
- The small portion of LLW not suitable for disposal in the national LLW repository
- Spent fuel from existing commercial reactors that is not yet reprocessed
- Spent fuel and ILW from new built nuclear programme
- Plutonium stocks (residual and not re-used in fuel fabrication)
- Uranium stocks
- Irradiated fuel and nuclear materials from UK defence programme.

As of 2013, the UK inventory accounts for 314,000 m³ of stored volumes, 466,000 m³ of conditioned volumes and 656,000 m³ of packaged volumes, with the ILW making up 90% of the total amount of waste. The projected waste and materials activity at 2040 will be dominated by SF and HLW, and at 2200 dominated by SF.
1.3 Geological Disposal of Nuclear Waste
A deep Geological Disposal Facility (GDF) is defined as a nuclear waste repository excavated deep within a geologically stable environment (below 200 metre, in accordance to the IAEA and NEA guidelines). It involves a four-stage integrated protection system including the waste form, waste package, an Engineered Barrier System (EBS) and the geological barrier (divided into a near-field and a far-field barrier). The repository is designed to seal the waste and protect the surrounding environment from any contaminants coming from the wasteform, so to impede the transport of radionuclides towards precious resources such as near-surface water reservoirs or soils and indeed the living environment.

Many of the 39 countries, which developed nuclear programmes in the past century, are now dealing with an increasing amount of nuclear waste and have focused their attention on interim or final disposal of their wastes in deep GDFs.

The most advanced programs are currently carried on by the Scandinavian countries, France and Switzerland, which have already identified potentially suitable areas or sites and have developed underground rock laboratories.

The technical concepts of the GDFs for the cited countries are based on simple assumptions:

- The area must be geologically stable and any possible future glacial period should not cause any disruption to the site.
- Host rocks should guarantee a complete isolation from the surface of the repository and hinder transfer of radionuclides.

Different countries have chosen different host rocks based on the peculiarities of the local geologies. For example, the French agency for the radioactive waste management (ANDRA) is investigating a site excavated in the claystones of the Callovo-Oxfordian formation of the Paris sedimentary basin at Bure (Meuse Department). Its Swedish counterpart SKB is operating a deep geological research facility in the Åspö HRL outside Oskarshamn [9] and plan to start building the world’s first GDF deep in the granitic rock underneath Forsmark in the municipality of Östhammar [10]. Granitic rocks belonging to the crystalline basements or cratonic areas have been chosen by SKB in Sweden, POSIVA in Finland (Onkalo) and ENRESA in Spain [11] and
sedimentary rocks by ANDRA in France [12], NAGRA in Switzerland [13], ONDRAF/NIRAS in Belgium [14] and COVRA in the Netherlands.

As previously stated, The UK policy is based on voluntarism. The siting process is divided into 6 stages [6]:

1. Invitation issued and Expression of Interest from communities
2. Consistently applied “sub-surface unsuitability” test
3. If an area has been identified as potentially suitable, the Community consideration leads to the decision to participate
4. Desk-based studies in participating areas
5. Surface investigations on remaining candidates
6. Underground investigation

So far, a number of communities (for example the Allerdale and Copeland districts, Cumbria, NW England) engaged with the process and participated in the early stages. However, no discussion proceeded further than stage 3, in 2013.

The GDF consists of a surface operational facility and the proper underground repository. The surface site will have buildings such as construction support and reception facilities, management and administration offices, workshops and a visitor center [15] (Figure 1-1). These structures will cover an area of approximately 1 km².

All the access ramps and shafts and depositional boreholes will be excavated deep underground (Figure 1-2), with two separate disposal modules in the concept, one for HLW and SF and the other for shielded and unshielded ILW/LLW [15] as illustrated in Figure 2. The footprint of the underground facilities, depending on the nature of the host rock, the quantity and the type of the waste could range between 6 and 26 km² (Figure 1-3).
The UK government policy also accounts also for the retrievability of the waste if it would turn out to be necessary to reuse it (in accordance with EUR 19145). CoRWM, acknowledging that a phased approach to disposal will give greater flexibility to future decision making, cautioned that ‘leaving a facility open, for centuries after waste has been emplaced, increases the risks disproportionately to any gains’ [15].
The waste disposal tunnels will host shafts in which the overpacked waste canisters will be emplaced into and then sealed. The sealing of the depositional shaft will happen differently for the HLW and the ILW, with the latter surrounded by an Engineered Barrier System (EBS) made by bricks of compacted bentonite clay and the former surrounded by a cementiferous backfill.

The planned lifetime of the GDF is of more than 100 years. After it is completely filled with waste, it will be sealed and closed, so the system in principle will eventually become completely water saturated and isolated from the surface.

1.4 The Engineered Barrier System and the SAFE Barriers project

One of the core features of all GDF concepts is the protection of the waste canisters from corrosion in order to guarantee the safety of the geosphere from any kind of contaminant possibly arising from the waste.

Hence, the national Nuclear Waste Management Organizations (WMO) have developed strategies for utilising a multi-barrier system.
The material constituting the EBS should be chemically inert with respect to the material the canister is made of and with the surrounding geosphere. The material of the EBS also needs to have a very low porosity and hydraulic conductivity, so the effects of any mechanical changes are minimized. Another important characteristic of the EBS material is its resilience to heating resulting from radioactive decay of the waste. The EBS material should not crack or swell with increasing temperature [6]. Most of WMO’s, including NDA, have focused on a three-level barrier system constituted by:

a. The metal canister in which the radioactive material is sealed. This can be a single layer of stainless steel with a thickness of about 12-15 cm [16] or a two-canister system composed by an inner container of nodular iron in a copper overpack, as in the Finnish concept [11]. For the UK concept of HLW disposed in hard fractured or “high strength” rock, the selected material is a non-magnetic 309L grade stainless steel.

b. Backfill/near-field material buffer. This comprises a thick layer (1 m) made of bricks of compacted bentonite (with a density of 1.76 kg/m³), which swells when it is exposed to groundwater. This swelling property is central as it is required to seal all the voids in the EBS and the fractures present in the adjacent host rock potentially formed or enhanced during the excavation process. The aim of the EBS is to form a continuous, low permeability medium around the waste packages (post water saturation), that limits the corrosion rate of the steel canister overpack and limits the transport of any potentially dissolved radionuclide or contaminant [12].

c. The final barrier is the geological barrier (geosphere) itself. The geological barrier can be divided in a near-field barrier (which will be affected by physical and chemical disturbance during the drilling process) and the far-field geological barrier (considered unaltered). The thickness of the near-field geological barrier depends on the nature of the host rock [17].

The SAFE Barriers (Systems Approach For Engineered Barriers) project, under which the research described in these thesis has been funded, is a ca. 1.3 million £ EPSRC consortium project led by Prof. Rebecca Lunn (University of Strathclyde).

The scientific objectives of the work packages within this consortium project are:
1. To deploy and refine advanced monitoring technologies for simultaneous imaging of THMC variables (pH, temperature, pore-water pressure, swelling etc.) within the laboratory.

2. To integrate these monitoring technologies with experiments to gain a predictive understanding of the THMC evolution of clay-based engineered barriers, and their interfaces, up to the upper bound of realistic environmental conditions.

The present project, within the SAFE Barriers Work Package 7 (WP7), relates to the scientific objectives at point 2.

1.5 EBS remote monitoring

A definition of monitoring of the disposal sites of HAW has been given in one 2001 IAEA report [18] as “continuous or periodic observations and measurements of engineering, environmental or radiological parameters, to help evaluate the behavior of components of the repository system, or the impacts of the repository and its operation on the environment”.

The importance of GDF and hence EBS monitoring was cleverly synthesized in the same report in the following statement: “The process leading to the commissioning of geological disposal facilities for long lived radioactive waste is quite lengthy and involves a number of decision points. (...) Monitoring of various aspects of the disposal system is likely to be an important support to decision-making at all stages of the
repository development programme. After closure, the long-term safety of geological disposal facilities, due to the duration of the hazard associated with the waste, cannot rely on institutional controls, including monitoring. However, continuing monitoring is likely to be a societal demand for some time after repository closure. Such monitoring, besides showing that the process of decommissioning surface facilities has been successfully completed, would also strengthen the confidence, at least in some sectors of society, that the evolution of the waste isolation system is in accordance with expectations. The need to safeguard nuclear materials contained in the repository may also cause some form of monitoring or surveillance to continue in the postclosure phase” [18].

Hence, remote monitoring of the waste canisters and also of the surrounding subsurface GDF environment is necessary not only to guarantee the safety of the repository but the safety of the operators throughout the lifetime of the repository and to increase the confidence and the reliance of the communities living in areas potentially affected by the repository over time.

The necessity of monitoring the GDF during its lifetime is taken into account by many national projects, but only some of these are considering the active monitoring post-closure [19]; the importance of pre- and post-closure monitoring of the GDF has been also recognized also by the IGD-TP Platform [20] and by the Modern2020 EC-project [21].

The safety of the environment is one of the points of main concern of the public. The excavation of the GDF and the emplacement of the waste will of course cause perturbation in the baseline levels of the original environment, so it is necessary to be able to gather fundamental data about bounding conditions such as groundwater flow field, geochemical characteristics of the groundwater and variations of radioactivity underground.

Collecting this data presents a significant technical challenge because the sensing techniques used must have the smallest impact possible on the stability of the barrier whilst providing data of reliable quality over prolonged timescales. Remote sensing techniques such as seismic, electric resistivity, magnetometry, gamma detection and georadar have been proposed as the most suitable for this as they do not require cables
within the EBS and can be easily performed, for example robotically, in the GDF pre-closure. However, although these are very good techniques for evaluating the changes in the geosphere, imaging the conditions of the boreholes or evaluating the behavior of the waste packages, they may not be able to provide reliable information on the many parameters that are useful for the evaluation of THMC (Thermo-Hydro-Mechanical-Chemical) coupling of the system over long timescales up to and including post-closure evolution.

Two of the work packages of the SAFE Barriers project seek to address this gap:

- Work Package 6: MEMS sensor monitoring technologies (Strathclyde University)
- Work Package 7: Magnetic Monitoring Materials (M³) (the University of Edinburgh)

1.6 Magnetic Monitoring Materials (M³) project

This PhD thesis focuses on the development of a materials-based magnetic monitoring system that has the capability to track the variations in groundwater ingress and solution chemistry throughout the repository lifetime and into post-closure. The initial concept to be investigated and evaluated is that a pre-designed and embedded magnetic system has the potential to monitor, through changes in the intrinsic magnetic field, the presence of fluids in the EBS.

The proposal is to embed magnetic materials / minerals within the EBS, in particular bentonite, both in close proximity to and further from the HLW/SF canister, and so register an easily measurable magnetic signal that can be monitored through time, as the magnetic properties of the system change as a consequence as reactive fluid ingress and saturation and, eventually, fluid composition, canister degradation and possibly radionuclide release.

The cartoon in Figure 1-5 summarizes the essential rock-fluid interaction and diffusion processes in an EBS, but does not take into account two important parameters: fluid salinity and pH. These two parameters play an extremely important role in the stability of the EBS bentonite buffer and in the corrosion processes taking place at the steel/bentonite interface, because highly saline solutions are widely recognized to enhance corrosion processes whereas increasing alkalinity causes passivation of the metal surfaces [22].
Salinity of the intrusive groundwater in a GDF is assumed to be essentially constant throughout time (around 0.5 times NaCl concentration in seawater) unless intrusion of brines from deeper reservoirs or the deep sea occurs, whereas alkalinity will increase at least over medium timescales due to interaction between groundwater and the cement/grout used to plug boreholes and deposition sites and to seal fractures present in the disturbed host rock (near field geological barrier). Even without considering the water/cement interaction, some models have predicted a significant increase of the porewater pH over a timescale between 100 and 100,000 years at the bentonite/steel interface due to the corrosion of the steel overpack [16].

The initial magnetic signature of the Engineered Barrier System (without any magnetic material embedded in the bentonite buffer) will be minimal [24] because the proposed stainless steel to be used to encapsulate the wasteform is a non-magnetic 309L stainless steel [25] that, however, carries tiny amounts of magnetic materials [24]. One of the processes that might change the magnetic signature of the EBS system in the absence of embedded magnets is the corrosion of the steel canisters. This can lead to the crystallization of magnetite on the steel surfaces, and is influenced by both temperature and pH [23] [16]. EBS evolution models foresee presence of a consistent magnetite layer (2cm) after around 10,000 years [16].

Figure 1-5: schematic representation of the fluid-rock interaction and solute diffusion in an EBS system, according to the French GDF concept (picture taken from [23])
The core idea of this project is to exploit the fluid-induced corrosion of either natural magnetic minerals or synthetic magnets to gather information on the progress of fluid saturation of the bentonite in an EBS and, in addition, on the geochemical properties of the fluids involved. The underlying assumption is that different fluid chemistries result in the evolution of different magnetic signatures due to the nature of the magnetic materials and their predisposition to corrosion in a given solution. This study offers an innovative use of mineral magnetism and is a first step in developing a new way forward for groundwater monitoring. It seeks to exploit magnet corrosion, which otherwise is one of the main limitations for their usage in many high-tech applications in “extreme” environments, to positively contribute to the complex challenge of EBS non-invasive remote monitoring.

In this thesis, the documentation and evaluation of corrosion-driven changes in magnetic properties is progressed in a two-stage experimental study of magnetic materials selected following a critic study of their relevant characteristics based on an extensive literature review.

The main characteristics considered in the choice of magnetic materials were:

- Commercial availability and cost
- Strength of the magnetic field
- Corrosion timescale

1.7 Thesis outline

The layout of the thesis follows a two-stage experimental process, in which the list of candidate materials was progressively narrowed down to a final list of three magnet types that are proposed to be suitable for use in future studies.

The initial list comprised one natural magnetic mineral (Magnetite – Fe₃O₄) and four synthetic permanent magnets (Nd-Fe-B, SmCo, AlNiCo and Ferrite).

In Chapter 2, the current state of research on the materials relevant in this study is outlined.

In Chapter 3 details about the set-up of the experiments are provided, together with analytical procedures and challenges faced during all stages of this research.

In Chapter 4, the first set of experiments, called Batch Experiments, is described.

In these experiments, magnetic materials have been corroded under “extreme” conditions (either with or without bentonite matrix), in order to understand if they react
and so have the capability of monitoring a system under "less extreme conditions". Chapter 4 is divided in seven sections, of which five are focused each on a particular magnetic material, one on the changes in the clay matrix and one on the chemical analysis of the solutions. The batch experiments have been designed in order to be very simple in design and economical; however, a simple design often leads to very complicated results that represent a starting point for future experiments rather than a definitive answer to our initial research question.

Testing the reactivity of the materials and their possible usage was a key focus of the Batch experiments. These results will be of great help for designing more complex experiments, in the near and far future, and for the upscaling of the project. In the batch experiments the magnetic materials were tested in two different sets (with and without bentonite) and with three different types of solutions (deionized water, high-pH solutions and saline solutions) in a regime of free swelling with no confinement, free pH drift and no recharge of reactants. The time–dependent changes of the samples were not controlled in this experiment.

The second part of this research represents the natural refinement of the experiments, in which the applied conditions were more controlled and closer to a real “evolved” EBS.

Chapter 5 describes the results of the second set of experiments, called Confined Fluid Flow experiments. In these experiments, the magnetic materials retained after assessment of the Batch experiments have been embedded within bentonite matrix in experiments designed to have confined swelling and imposed fluid flow. The solution used was a 0.273M NaCl solution reacted with NRVB cement to increase its pH to 12, and purged with N₂ gas, to simulate a solution in a subsurface alkaline plume interacting with the EBS. Three stacks of reaction vessels were prepared and extracted at intervals of 4 months to study the evolution of the magnetic system with time. This chapter is divided into 4 sections, of which 3 focused on the magnets and one on the clay matrix.
2 Background: research on clays and magnetic materials

In this chapter, the state of the art of research in clay science, permanent magnets and natural magnetic materials is reviewed. This chapter presents a broad review on the research on the materials used in this research, from their crystallography, to the latest developments on corrosion processes and their effects.

Clays have always been extremely important industrial materials since the first civilizations appeared. Their applications have spanned from pottery to masonry and beauty products, but today there is increasing scientific interest in their thermo-mechanical-chemical properties, which make them very useful materials for applications in health science, engineering and material science.

Magnetite has been the subject of extensive studies throughout the history of modern science, for its importance as an ore mineral (it is the main ore mineral for iron) and it is the main mineral for paleomagnetic analysis. During the second part of the 20th century magnetite has played an important role in corrosion science (it is the main corrosion product of steel) and has become of interest as possible adsorbent of contaminants (hazardous metals) in mine tailings [26].

Over the past few decades, research on the development of new permanent magnets has been promoted by the singular importance of these materials for a vast range of industrial and civil applications, ranging from informatics to medical technologies and space industry. These synthetic magnets are gaining even more importance with the increasing quest to increase renewable energy in global electricity production.

Research on corrosion studies of permanent magnets has increased in importance in the light of increasing demand of electric engines for fuel-free cars, turbines for windfarms and green energy power plants. Corrosion kinetics and their dependence on temperature and environmental conditions (especially in humid environments) have been extensively studied [27] [28] [29] [30] [31]. However, less work has been done on the corrosion in wet environments and in saturated and unsaturated soils.

The use of these magnets as water chemistry monitors through the evolution of their magnetic properties has so far not been considered, so this study can be regarded as initiating a new branch of research that connects remote sensing with water geochemistry and materials science.
2.1 Clays and Na-montmorillonite

Clays are widespread rock- and soil-forming minerals, belonging to the phyllosilicate mineral species. Clays are very important industrial minerals, being used for the production of ceramics, paints, industrial adsorbents and cleaning products and they have several applications in environmental protection issues. In this research program, they are relevant as bentonite (Na-montmorillonite) will be used as a major component of the engineered barrier because of its swelling properties and low hydraulic conductivity.

Clay is a rock term and, like most rocks, clay is made up of a number of different minerals in varying proportions. The word clay refers to a naturally occurring material mainly composed of fine-grained minerals, which is generally plastic at appropriate water contents and hardens when dried or fired [32, 33]. Moore [34] suggested that the word “clay” can signify a rock, a sedimentary deposit, and the alteration (weathering) products of primary silicate minerals; it is in all of these senses that the term ‘bentonite’ has been used in the literature.

Clays are phyllosilicates with the main feature that the silica polyhedrons (T site) share 3 vertices with other tetrahedrons (T), forming sub-layers of 4-coordinated polyhedrons; the other vertices are shared with an octahedron (M site). Octahedrons share vertices and edges with other octahedrons, forming sub-layers of 6-coordinated polyhedrons: one or two vertices are shared with tetrahedrons, depending on the type of package (Figure 2-1).

The octahedral sheets (Figure 2-1) can be described as composed of two planes of close-packed hydroxyls with cations occupying the octahedral sites between the two planes [35].

Clays have three types of sub-layer packaging (or layer composition): T-O, T-O-T or T-O-T-O, which are divided by highly coordinated cations (12-coordinated polyhedron or A site), such as Ca$^{2+}$, Na$^{2+}$ or K$^+$, or by H$_2$O. The tetrahedrons are commonly occupied by silica, however, they can occasionally accommodate aluminium; the octahedrons accommodate trivalent cations such as Fe$^{3+}$ and Al, but they can contain also magnesium. The unit cell of the 2:1 (T-O-T) phyllosilicates (e.g. Na-Montmorillonite) contains contains six octahedral sites and eight tetrahedral sites [36].
Substitution of Si$^{4+}$ with R$^{3+}$ in tetrahedral sites generates an excess of negative charge on the three basal oxygens and the apical oxygen. This affects the total charge of the 2:1 layer as well as the local negative charge at the layer surface. Al$^{3+}$, Fe$^{3+}$, Mg$^{2+}$, Fe$^{2+}$ generally occupy the octahedral sites.

The population of the octahedral sheet is another very important feature, because it allows division of the clay minerals into dioctahedral and trioctahedral clays. The general formula for a dioctahedral phyllosilicate is $\text{A}_{0.3}\text{M}_2[\text{T}_4\text{O}_{10}]\text{Z}_2^*\text{nH}_2\text{O}$ (where M is the octahedral site occupied only by trivalent ions and Z the hydroxyl group OH$^-$), whereas the general formula for a trioctahedral phyllosilicate is $\text{A}_{0.3}\text{M}_3[\text{T}_4\text{O}_{10}]\text{Z}_2^*\text{nH}_2\text{O}$ (where M is the octahedral site occupied only by bivalent ions). Commonly, clay minerals present a mixed octahedral layer, in which both bivalent and trivalent ions are present ($\text{A}_{0.3}\text{M}_{2-3}[\text{T}_4\text{O}_{10}]\text{Z}_2^*\text{nH}_2\text{O}$).

Brigatti et al. [36] provide a structural definition of dioctahedral and trioctahedral phyllosilicates and of the 1:1 and 2:1 layer structures; structures with all the six octahedral sites occupied are called trioctahedral, whereas structures with only half of the octahedral sites occupied are known as dioctahedral. The structural formula is often reported on the basis of the half unit-cell content. In dioctahedral smectites, substitution of divalent cations in the octahedral site creates an excess of negative layer (TOT) charge.

Na-montmorillonite belongs to the smectite group, which is composed by dioctahedral expandable clays with a TOT layer composition (Figure 2-1). Commonly Si$^{4+}$, Al$^{3+}$ and Fe$^{3+}$ are found in tetrahedral sites.

Most of the technological uses of smectite are related to what happens in the interlayer space. Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$, which balance the negative 2:1 layer charge, are found in this interlayer and are commonly hydrated and exchangeable. Smectites contain water in several forms. There can be porewater (which can be easily removed by air-drying) but water can also be associated with layer surfaces and interlayer space.
Usually, three models [37] of hydration (recognized to be pH dependent) are distinguished:

1. Interlayer hydration (of internal surfaces) of primary clay mineral particles
2. Continuous hydration relating to an unlimited adsorption of water on internal and external surfaces
3. Capillary condensation of free water in micropores

The main features controlling interlayer hydration [38] are:

1. Hydration of interlayer cations
2. Interaction of clay surfaces with water molecules and interlayer cations
3. Water activity in the clay-water system

![Figure 2-1: Montmorillonite 3D stick-and-ball crystal structure][35]

The interlayer hydration complexes of smectites, arising from intercalation of a discrete number of water layers, can be distinguished by X-ray or neutron diffraction. This number ranges from zero to three, corresponding to the formation of zero-, one-,
two- or three-layer hydrates. The main factors affecting the interlayer hydration of smectites are [37]:

1. Hydration energy of the interlayer cation (zero for K⁺) [39]
2. Polarization of water molecules by interlayer cations
3. Variation of electrostatic surface potentials because of differences in layer charge location [40]
4. Activity of water [41]
5. Size and morphology of smectite particles

Swelling of smectite occurs in a stepwise fashion, through the sequential formation of integer layer hydrates, and hence may be viewed as a series of phase transitions between such hydrates. In Na⁺-exchanged smectites each Na⁺ ion is surrounded by five water molecules, while its position depends on the layer charge location. In montmorillonite, Na⁺ is located above the hexagonal cavity just over the octahedron in which Mg²⁺ substitutes for Al³⁺.

Water shows a strong preference to forming an intermolecular hydrogen-bonded network, while the hydrogen bonds to the alumosilicate surface are weak and short-lived. The location of isomorphous substitution in the layer (whether the layer charge derives from substitution in the tetrahedral or octahedral sheet) is an important factor affecting smectite hydration.

An expansive smectite particle comprised of two unit layers undergoes four successive stages of hydration (Figure 2-2), starting with a completely dry system and hydrating up to three molecular layers of water.
As water is absorbed in the interlayer, the mineral basal spacing makes a transition to the next hydrate state. According to Karaborni et al. [43], the basal spacing of smectite proceeds from 9.7 Å to 12.0 Å upon transitioning from the zero-layer state to the one-layer hydrate, from 12 Å to 15.5 Å during the one-layer to two-layer transition, and from 15.5 Å to 18.3 Å during the two-layer to the three-layer transition. For hydrating sodium smectite, relative humidity values (RH) corresponding to the successive hydration regimes range from approximately 30% to 60% for stability of the one-layer hydration state, and 75% and greater for the two-layer hydrate state [44].
2.1.1 Alteration of Na-montmorillonite

Previous studies on smectite transformations have been carried out with saline and K-rich solutions, to evaluate the influence of water composition on swelling capacity [45][46]. In the last two decades, with the increasing interest on the engineering application of bentonite, the interactions with cements or grouts were investigated.

Kaufhold & Dohrmann [47] studied Na-montmorillonite stability in hypersaline conditions (6M NaCl solution). The resultant XRPD traces showed a reflection shift of the air-dried smectite peak that initially was centred at 14.8 Å with a pronounced shoulder at 12-13 Å. The asymmetry was related to a non-uniform cation saturation. After EG (Ethylene-Glycol) saturation both reflections were at the same position but the basal reflections showed a broadening when compared to the initial sample recorded under the same conditions.

Herbert et al. [45] studied the interactions between bentonite and highly saline fluids that would occur in salt-hosted deep underground HLW repositories in Germany (excavated in salt domes, comparable to Goreleben [11]). They also compared the results with the existing data gathered on natural bentonites from the East Slovak Basin studied in several drill holes down to 4000 m depth [46]. Sucha et al. [46] found that the salt-bearing natural bentonites suffer a significant loss of expandability at shallower depth (ca. 1.5 km) if compared to the salt-free bentonites, but at greater depths (3 km) their values become comparable.

Herbert et al. [45] found that montmorillonite is the dominant phase in all reaction products, but also that the typical particle shape of Wyoming montmorillonite was completely altered in all finely dispersed particles of the reaction products. In the diffractograms they found no difference of intensities or broadening of the peaks. The only difference noted was with respect to that reduced octahedral charge, which resulted in a loss of interlayer charge and a consequent decrease in water uptake capacity.

In contrast to Na\(^+\), K\(^+\) is known to play a significant role with respect to smectite alteration because K\(^+\) can form anhydrous complexes with basal oxygens because its hydration enthalpy is low [48]. The final stage of K\(^+\) adsorption is the formation of a collapsed layer (\(\approx10\text{Å}\)). This behaviour is only observed in the case of K\(^+\) being the
exchangeable cation and can be explained by the lower hydration energy and from steric principles (diameter of K$^+$ fits particularly well with the dimensions of the ditrigonal cavity [49]). K fixation is regarded as an initial step towards illitization although the actual mechanisms of illitization still are a matter of considerable debate [50]. According to Lee et al. [51] there are two important mechanisms:

- Layer by layer (solid state) transformation [52]
- Dissolution/precipitation [53]

Little argument exists that illite is energetically more stable in the presence of K$^+$ in solution, but some authors point out that, based on the Gibb’s phase rule, the transformation of smectite has to be described by a disequilibrium model [54]. According to Eberl et al. [55] the illitization of smectite takes place at high temperatures or high pH levels; the latter promotes smectite dissolution even at low temperature resulting in illitization by dissolution and precipitation. The product has a basal spacing $\approx$10Å, typical of illite/muscovite and hence indicates the presence of illite.

According to Hower & Mowatt [56] there is no correlation between the composition of the octahedral layer with the increasing percentage of mixed-layer illite, although some other authors [57] reported a correlation.

According to Garrels [58], in nature, a typical layer of K-montmorillonite is transformed to a typical illite layer by a process with a stoichiometry such as the following:

\[
\text{Equation 2-1: } K^+_{0.33}(\text{Al}_{1.5}\text{Fe}^{3+}_{0.23}\text{Mg}^{2+}_{0.27})(\text{Al}_{0.06}\text{Si}_{3.94})\text{O}_{10}(\text{OH})_2 + 0.47\text{KAlSi}_3\text{O}_8 = K^+_{0.8}(\text{Al}_{1.5}\text{Fe}^{3+}_{0.23}\text{Mg}^{2+}_{0.27})(\text{Al}_{0.53}\text{Si}_{3.47})\text{O}_{10}(\text{OH})_2 + 1.88\text{SiO}_2
\]

Kaufhold & Dohrmann [50] also studied the behavior of several smectite samples altered in the presence of KCl saturated liquids, demonstrating that they suffer a significantly higher loss of swelling capacity compared with smectites altered by NaCl saturated fluids [47]. This loss corresponds to the decrease of the water uptake ($\approx$50%). The decreased swelling capacity has been explained by the layer density (the greater the layer charge density the higher the loss of swelling capacity).
Kaufhold & Dohrmann [59] studied the interactions between bentonite and Ca(OH)$_2$-saturated solution, with one batch experiment carried out at 60°C and the other at 90°C. The experiment at 60°C did not lead to any significant smectite alteration, and no correlation was observed between silicate dissolved during that experiment and that measured in the KCl experiment [50]. The experiment at 90°C led to the precipitation of a relatively constant amount of carbonate in every sample. The XRPD traces confirmed the precipitation of calcite and aragonite. Kaufhold & Dohrmann [59] concluded that bentonite reacted with Ca(OH)$_2$ solutions, bentonites undergo alteration controlled by dissolution/reprecipitation mechanism.

Some modelling studies have focused on the interaction between hyperalkaline fluids and bentonite, because concerns exist on the stability of bentonite buffer in presence of hyperalkaline pore fluids (pH higher than 12) characteristic of cement and cementitious grout.

From the estimations of Cuevas et al. [60], a 30 cm thick OPC (Ordinary Portland Cement) block generates high pH leachates capable of partially altering 5 mm of compacted bentonite, and similar thicknesses were identified where hyperalkaline fluid was percolated through compacted bentonite with forced advection at 120°C [61]. At room temperature, the precipitation of poorly crystalline phases decreased advective transport [61] and no changes were detected below the first mm from the interface. In that study, it was demonstrated that Ca$^{2+}$ adsorption in the bentonite interlayer in the reaction zone is almost independent of linear velocity, temperature and type of percolating fluid. This implied that Ca$^{2+}$ concentration gradient depends on diffusive transport through the montmorillonite interlayer. Fernandez et al., [61] concluded that Ca$^{2+}$ concentration gradient moves by diffusion dominated transport instead of the imposed advective flow.

A vast literature on clay/cement interactions exists both on experimental research [55, 62, 63, 61, 64] and modelling of the short- and long-term interface reactions [65, 66, 67]. However, there are still uncertainties about the behaviour of bentonite under lower alkaline pH (ca. 12), and on the phases that might form at lower temperatures and the transformations occurring to the montmorillonite with time.
All these studies on montmorillonite under highly alkaline conditions noted three relevant common points [64]:

1. Montmorillonite dissolves in hyperalkaline conditions (thanks to the high pH cement porewater) precipitating zeolites and leaving residual clays.
2. Bentonite buffers the pH from 13-13.6 to 12.5 (if OPC is used) and portlandite is dissolved at the interface forming calcium-silicates hydrates (CSH) phases.
3. Part of the dissolved Ca\(^{2+}\) is incorporated in the bentonite.

Fernández et al. [64] found that in the alteration area a complex mixture of disordered clays was present, with zeolites inferred from EG-samples (merlinoite or phillipsite) whereas at greater distance from the interface the exchange of Mg by K or Na was more evident, suggesting pH buffering at the interface.

Dissolution of clays at the cement/bentonite interface is known to be a pH-limitating effect within the bentonite barrier [68]. However, the dissolution of the accessory minerals also has to be taken into account because can have an important role as pH-buffer favouring the precipitation of zeolites, CSH and C(A)SH phases.

Bentonite-cement interaction is difficult to model due to the fact the precipitation of secondary minerals can either promote or stop matrix alteration and as it also is not considered a simple and linear system [69]. To add further complexity to the modelling, the thermodynamic properties of calcium-aluminium silicate hydrates (CASH) are not well known. Savage et al. [69] modelled the alteration mechanisms of bentonite by alkaline fluids and reviewed the role of the secondary minerals. He found that at lower pH more siliceous zeolites (clinoliptonite and phillipsite) form, whereas at higher pH C(A)SH phases, illite, feldspars and alluminous zeolites (analcime and heulandite) are likely to form.

With increasing activity of Al(OH)\(_4^-\) in solution, phases like hydrogrossular (Ca\(_3\)Al\(_2\)Si\(_2\)O\(_8\)(OH)\(_4\)) may form in the clay matrix [69] [70]. Kubo et al. [71] studied bentonite interaction with hyperalkaline fluids in the temperature range 50-100°C, finding that calcium-aluminium hydrate and CSH phases were present at pH 12.5 but not at pH 11.5. Kuroki et al. [72] in a experiment run in a similar fashion to Kubo et
al. [71] but of two years duration discovered complete replacement of montmorillonite by CSH and C(A)SH phases at pH 11.5 and 70°C, but no alteration of montmorillonite at pH 10.5. Savage [65] stated that zeolites are likely to crystallize at lower pH than C(A)SH phases and where there is an appreciable amount of Al and Si in solution. However, zeolite stability also depends on silica activity in solution [73] [74], and, in the case of bentonite-cement system at high pH, silica is most likely saturated or supersaturated with respect to quartz [75]. As a consequence, those zeolites stable in silica undersaturated media (scolecite, mesolite, scolecite, natrolite and stilbite) are not thought to occur during cement-bentonite interaction [69].

Savage et al. [69] also found the following results on bentonite/cement interaction, of relevance to this specific project:

- Cement pore fluid composition changes with time
- Many secondary minerals can be poorly crystallized or metastable solid solutions

In recent years, the interaction between smectite and iron also has been studied extensively, because the transformations induced to the bentonite matrix in a Fe-rich environment may cause significant losses of swelling capacity resulting from crystallization of non-swelling phyllosilicates like chlorite or berthierine.

Guillaume et al. [76] experimentally investigated the transformations occurring in smectite in presence of Fe oxides and NaCl-CaCl2 low salinity solutions at 80°C and 300°C. Their results show clearly that no change, or formation of nontronite, occurs to the clay at 80°C. On the other side, at 300°C, the nine-month long experiments led to the formation of Fe-saponite, quartz, feldspar and zeolites.

Charpentiera et al. [77] studied MX-80 bentonite/iron interactions under alkaline conditions (pH 12.35) at 80, 150 and 300°C and found that at 80°C XRPD traces are similar to the initial material. At 150°C no changes were detected either, despite pronounced shoulders at lower diffraction angles in the air-dried XRPD traces. At 300°C, they found that a swelling clay remains the dominant phase, accompanied by secondary phases, possibly illite/montmorillonite or illite/vermiculite material. Charpentiera et al. [77] also found that the timescale of the experiment greatly
influences the Fe increase and Al decrease in the clay and so the evolution from low-charge montmorillonite to saponite or mixed montmorillonite/vermiculite layers.

Mösser-Ruck et al. [78] studied the impact of T, liquid/clay and iron/clay ratios on the transformations of montmorillonite and found that at 80°C the duration of the experiment had no effect on the reaction, whereas the increasing iron/clay ratio led to formation of 7Å clay (berthierine) or mixtures of smectite and 14Å chlorite. At 300°C, they observed Si depletion and Fe enrichment, the last one particularly high at high iron/clay ratios. At 300°C, crystallization of saponite was detected, with vermiculite as the predominant mineral, whereas at temperatures lower than 150°C a 7Å phase mixed with the starting smectite was detected. Regardless of chemical constraints or iron/clay or liquid/clay ratios in all samples, a chemical/mineralogical zoning was observed from the iron/bentonite interface to the bulk bentonite (decrease in Fe and increase in Mg in the clay). Similar chemical zoning was also reported by Milodovsky et al. [79].

The interaction between Fe pellets and gels of different types of bentonites was studied by Kaufhold et al. [80]. In a month-long experiment with water at 60°C, they identified new XRPD peaks related to berthierine as a corrosion-related product but also an additional intensity at ca. 19°2θ that was related to another corrosion-related product. In their other experiments conducted with other varieties of bentonite, Kaufhold et al. [80] found that corrosion is enhanced when the iron pellets were embedded in gels of more Ca-rich montmorillonites, confirming the higher corrosivity of Ca-montmorillonites.

From the summary of the results of previous studies on bentonite/cement (Table 2-1) and bentonite/iron interaction (Table 2-2), it is visible how results are variable depending on experimental conditions and starting materials.
Table 2.1: Summary of the results of experimental and modelling works on bentonite/cement interaction relevant to this thesis.

<table>
<thead>
<tr>
<th>Author (year)</th>
<th>Experimental</th>
<th>Starting material</th>
<th>Water composition</th>
<th>Temperature</th>
<th>Reaction phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuevas (2004)</td>
<td>Yes</td>
<td>FEBEX montmorillonite</td>
<td>NaOH 0.1 M, 0.25 M, 0.5 M + Ca(OH)$_2$ at saturation</td>
<td>25, 75, 125, 200°C</td>
<td>Analcime, tobermorite (CSH gel), gyrolite, phillipsite, saponite</td>
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<tr>
<td>Fernandez et al. (2006)</td>
<td>Yes</td>
<td>FEBEX montmorillonite</td>
<td>Ca(OH)$_2$-saturated</td>
<td>25, 60, 120°C</td>
<td>Tobermorite (CSH), Mg-silicate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FEBEX montmorillonite</td>
<td>0.25 M NaOH</td>
<td>25, 60, 120°C</td>
<td>Analcime</td>
</tr>
<tr>
<td>Fernandez et al. (2009)</td>
<td>Yes</td>
<td>Mg-saturated FEBEX montmorillonite</td>
<td>Hyperalkaline (Ca-, K-, Na-rich)</td>
<td>60°C</td>
<td>Disordered clays (merinocite/phillipsite gibs, brucite)</td>
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<tr>
<td>Sanchez et al. (2006)</td>
<td>Yes</td>
<td>FEBEX montmorillonite</td>
<td>Hyperalkaline (0.1-0.5 NaOH in presence of portlandite)</td>
<td>25, 75, 125, 200°C</td>
<td>Analcime and tobermorite (120-200°C) Amorphous CSH (25-75°C) Phillipite (75°C)</td>
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<td>Eberl et al. (1993)</td>
<td>Yes</td>
<td>Na-montmorillonite</td>
<td>Hyperalkaline (0.5 M NaOH)</td>
<td>35°C</td>
<td>Random mixed-layer phyllosilicates containing non-expandable clays</td>
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<td>Savage et al. (1997)</td>
<td>No</td>
<td>Na-montmorillonite</td>
<td>Hyperalkaline (pH 11-12)</td>
<td>25, 70°C</td>
<td>Clinoptilite/phillipsite</td>
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<td></td>
<td></td>
<td></td>
<td>Hyperalkaline (pH 12-14)</td>
<td>25, 70°C</td>
<td>C(A)SH, illite, feldspars (analcime/portlandite)</td>
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<td>Kubo et al. (1998)</td>
<td>Yes</td>
<td>Ca-Na Montmorillonite</td>
<td>Hyperalkaline (pH 11-13)</td>
<td>50-100°C</td>
<td>C(A)SH and CSH at pH 12.5 No reaction phases at 11.5</td>
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<td>Kuroki et al. (1998)</td>
<td>Yes</td>
<td>Ca-Na Montmorillonite</td>
<td>Alkaline (pH 10)</td>
<td>70°C</td>
<td>No alteration at pH 10.5</td>
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<td></td>
<td>Hyperalkaline (pH 12)</td>
<td>70°C</td>
<td>CSH and C(A)SH at 11.5</td>
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<td>Savage et al. (2002)</td>
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<td>Na-montmorillonite</td>
<td>Hyperalkaline (pH 12.7, equilibrium with Ca(OH)$_2$)</td>
<td>70°C</td>
<td>Tobermorite, analcite, celadonite, leucite</td>
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<td>Hyperalkaline (pH 11.2, equilibrium with CSH gels)</td>
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<td>25°C</td>
<td>Tobermorite, K-clinoptilite, illite, Ca-saponite, clinohlore</td>
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Table 2-2: Summary of the results of experimental and modelling works on bentonite/iron interaction relevant to this thesis.

<table>
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<tr>
<th>Author (year)</th>
<th>Experimental</th>
<th>Starting material</th>
<th>Water composition</th>
<th>Temperature</th>
<th>Reaction phases</th>
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<td>Madsen (1998)</td>
<td>Yes</td>
<td>Na-montmorillonite + Fe or magnetite powders</td>
<td>Water vapour</td>
<td>80°C</td>
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<td>Guillaume et al. (2004)</td>
<td>Yes</td>
<td>Na-montmorillonite + Fe or magnetite powders</td>
<td>NaCl-CaCl₂ low salinity solutions</td>
<td>80°C</td>
<td>Nontronite</td>
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<tr>
<td></td>
<td>Yes</td>
<td>Na-montmorillonite + Fe or magnetite powders</td>
<td>NaCl-CaCl₂ low salinity solutions</td>
<td>300°C</td>
<td>Chlorite and Saponite</td>
</tr>
<tr>
<td>Charpentier et al. (2006)</td>
<td>Yes</td>
<td>Na-montmorillonite + Fe or magnetite powders</td>
<td>Hyperalkaline (pH 12.5)</td>
<td>80°C</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-montmorillonite + Fe or magnetite powders</td>
<td>Hyperalkaline (pH 12.5)</td>
<td>150°C</td>
<td>None</td>
</tr>
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<td>Mösser-Rack et al. (2010)</td>
<td>Yes</td>
<td>Na-montmorillonite + Fe powders</td>
<td>Alkaline and Hyperalkaline</td>
<td>80°C</td>
<td>Berthierite or Chlorite (influenced by iron/clay ratio)</td>
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<td></td>
<td>Yes</td>
<td>Na-montmorillonite + Fe powders</td>
<td>Alkaline and Hyperalkaline</td>
<td>150°C</td>
<td>7A clay phase</td>
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<td>Yes</td>
<td>Na-montmorillonite + Fe powders</td>
<td>Alkaline and Hyperalkaline</td>
<td>300°C</td>
<td>Saponite and Vermiculite</td>
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<td>Kaufhold et al. (2015)</td>
<td>Yes</td>
<td>Ca- and Na-montmorillonite + iron pellets</td>
<td>Water</td>
<td>60°C</td>
<td>Berthierite</td>
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</table>
2.2 Permanent neodymium magnets

The most widely used rare-earth magnets are the so-called Nd-Fe-B or neo-magnets, which are permanent magnets made from an alloy of boron, iron and neodymium. Their simplified general formula is Nd₂Fe₁₄B.

In 1982, General Motors (GM) and Sumitomo Special Metals discovered the Nd₂Fe₁₄B compound. The research was initially driven by the high raw materials cost of SmCo permanent magnets, which had been developed earlier. GM focused on the development of melt-spun nanocrystalline Nd₂Fe₁₄B magnets, while Sumitomo developed full density sintered Nd₂Fe₁₄B magnets.

GM commercialized its inventions of isotropic Neo powder, bonded Neo magnets, and the related production processes by founding Magnequench in 1986 (Magnequench has since become part of Neo Materials Technology, Inc., which later merged into Molycorp). The company supplied melt-spun Nd₂Fe₁₄B powder to bonded magnet manufacturers. The neodymium iron boron (Nd-Fe-B) magnets were first commercially available in 1984. Neodymium magnets were initially developed for voice coil motors in computer hard disk drives and this market still accounts for over 50 percent of all Neodymium magnets produced. Other applications include high performance motors, brushless DC motors, generators, magnetic separation, magnetic resonance imaging, sensors and loudspeakers.

The tetragonal Nd-Fe-B alloy structure has an unusually high uniaxial magnetocrystalline anisotropy, which gives the compound a high resistance to demagnetization and a very high saturation magnetization. The Maximum Energy Product (BHmax) of the commercial grade NEO-magnets ranges from 27 MGOe to 52 MGOe (N27 to N52) and with a maximum operating temperature rating ranging from +60/+80°C to +220/+230°C.

Nd-Fe-B magnets contain 60-75% iron (amount is dependent on grade) and are therefore prone to corrosion. Protective coatings are applied to Nd-Fe-B magnets; the most common one is an electroless nickel plating (Ni-Cu-Ni; effectively a triple coating).
According to Sagawa et al. [81] amongst a number of ternary compounds synthesised composed of LREE, Fe and small quantities of a third element a remarkable compound of Nd, Fe and B was discovered. This phase forms near the composition 12% Nd, 82% Fe and 6%, having a tetragonal crystal structure. The approximate composition of this magnet is Nd$_{15}$Fe$_{77}$B$_8$. The magnetic phase has a Curie temperature of 585 K, saturation magnetization more than 1.3 T and a first order magnetocrystalline anisotropy constant amounting to 3.5 MJ/m$^3$ with the easy axis parallel to the c-axis of the tetragonal unit cell. The coercivity is 1.23 T, remanence 145 Am$^2$/kg and maximum energy product of 290 kJ/m$^3$ [81].

In an Nd-Fe-B alloy three phases can be defined (Figure 8). The matrix is made of a ferromagnetic tetragonal Nd$_2$Fe$_{14}$B phase ($\varphi$-phase) and is surrounded by intergranular regions containing a neodymium-rich phase ($\rho$-phase) Nd$_2$Fe$_7$B$_6$ [82] [83] and a B-rich phase ($\eta$) Nd$_{1+x}$Fe$_4$B$_4$ [84] [85].

1. The $\varphi$-phase, which is the main magnetic phase, forms most of the granular material (Figure 2-4). Using a CBED pattern it was found that there exist two mirror planes perpendicular to the l and h axis, so this indicates that the point
group is 4/mmm and the corresponding space group is P42/mnm [81]. From the
density 7.55 Mg/m³, the analysed composition of Nd₁₂Fe₈₂B₆ for cast magnets
and the space group P42/mnm, Sagawa et al. concluded that every single unit
cell contains 8 Nd, 56 Fe and 4 B atoms, and so the formula for this tetragonal
compound is Nd₂Fe₁₄B. The XRPD pattern exhibits the typical intensity
distribution in the (hk0) reciprocal plane with very strong 410, 330, 550, 720,
820 and 660 reflections (Figure 2-3).

Figure 2-4: Nd-Fe-B magnets microstructure (Schultz et al. [86])

2. The η-phase, with a formula Nd₁₊ₓFe₄B₄, is found only in certain areas but its
presence appears not to be related to grain boundaries [84] [85].
3. The ρ-phase (formula Nd₂Fe₇B₆) is found along the grain boundaries [87] [83]
and its presence is related to the metallurgical process; this phase may be lost
during the polishing process due to its chemical reactivity. The ρ-phase is
found along the grain boundaries in the matrix and has a tetragonal structure
with a=0.716nm and c=0.391nm with an fcc structure [81]. Holc et al. [82]
described the ρ-phase as an amorphous compound in which fades in the hard
magnetic φ-phase through an intermediate transitional phase which exhibits
main peaks (labelled 140 and 330) corresponding to values obtained by x-ray
diffraction on a Nd$_2$Fe$_{14}$B alloy. The diffraction pattern of the $\rho$-phase shows only one peak with $d=0.3\text{nm}$ (reflection at 30° 2$\theta$ in Figure 8).

Several studies have demonstrated the dependency of the coercivity of Nd-Fe-B alloys on the grain size of the $\phi$-phase [88] [89] [90] and on the initial powder particle size [91]. Generally, Nd-Fe-B alloys with very high coercivity (Hc or Bc) have small mean grain size of the main magnetic phase $\phi$ [88]. This occurs because smaller grains have a lower probability of strong surface defects and so achieve higher coercivities [91].

Although coercivity increases with decreasing grain size of the $\phi$-phase, Christodoulou et al. [92] stated that there is a critical value below which the coercivity decreases with further particle refinement. Christodoulou et al. [92] found that the coercivity of industrial Nd-Fe-B alloys decreased greatly with the average grain size of the $\phi$-phase is less than 3 $\mu$m. This decrease is ascribed to the effect of surface oxidation of finely milled powders, which increases the volume fraction of Nd oxides in the material and so suppresses the formation of the $\rho$-phase during the sintering process.

In modern industrial high-precision Nd-Fe-B magnets, the formation of Nd oxides during the powder milling is prevented by jet-milling the powders under nitrogen and argon atmosphere and sintering the powders under a controlled oxygen atmosphere [93]. This ensures high coercivity for even finely-milled powders.

The experiments in this study have used N42 grade Ni-Cu-Ni coated Nd-Fe-B (produced by e-magnetsUK). This magnet type is produced by sintering a powder in a mould with a solenoid coil set either side of the compacted powder yielding an external magnetic field that allows the magnetic domains to align to give a perfect magnetic anisotropy (source: http://www.ndfeb-info.com).

The microstructural relationship between the three main components of Nd-Fe-B magnets is essential to understand the corrosion kinetics and products because the three phases have different chemical activities and this can hence lead to high potential differences between the matrix and the intergranular phase [28] when in humid or aqueous environments.
2.2.1 Nd-Fe-B alloys corrosion in humid or aqueous media

Several studies relate the corrosion properties of these alloys with the magnets microstructure [86], [27], [29], [28] and others point out the important role played by hydrogen [84] [94] [95] [96].

The corrosion of Nd-Fe-B magnets can cause a worsening of their magnetic properties, loss of mechanical properties, and sometimes disaggregation of the magnets to fine powders. These effects are mainly related to the presence of the multiple phases within the magnet and their completely different electrochemical properties.

The main reason for the low corrosion resistance of these magnets is the fast oxidation, even in air, of the Nd- and B-rich phases located around the φ-phase grains. This arises because the REE represent some of the most chemically active metals (standard electrode potentials \( E^0 \) are between -1.9 and -2.5 V [97] [86] [85]). Sugimoto et al. [98] studied the corrosion rates of the three phases in a neutral borate-boric acid buffered solution and found that these increase from the φ-phase to the η-phase. This means that the η- and subsequently the ρ-phase dissolve preferentially, resulting in localized intergranular corrosion, which continues until the φ-phase grains break apart, creating a disaggregated powder [86]. The ρ-phase on the surface of the magnets reacts with water vapour and oxygen in a hot, humid atmosphere as in Equation 2-2 [28], with hydrogen generated from the decomposition of water vapor reacting with the Nd [85] [95].

\[
\text{Equation 2-2:} \quad \text{Nd} + 3\text{H}_2\text{O} \rightarrow \text{Nd(OH)}_3 + 3\text{H} \quad [85]
\]
\[
\text{Equation 2-3:} \quad \text{Nd}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Nd(OH)}_3 + 3\text{H}^+ \quad [85]
\]

The resultant hydrogen then diffuses into the magnet along grain boundaries and becomes a reactant with the ρ-phase [95], causing the observed corrosion [95] [28]:

\[
\text{Equation 2-4:} \quad \text{Nd} + 3\text{H} \rightarrow \text{NdH}_3
\]

The volume expansion of the ρ-phase along the grain boundaries results in the dislodgement or exfoliation of the grains of the φ-phase, which form separate powderized granules (Figure 2-5) [86]. Additionally, electrochemical corrosion will occur in Nd-Fe-B magnets in a high humidity atmosphere. This happens because a corrosion microbattery forms when there is water on the surface of the magnet, owing
to the corrosion potential difference between the $\varphi$-phase and the $\rho$-phase (they are electrochemically coupled and the material with the highest galvanic activity is the first to corrode).

![Figure 2.5: Schematic illustration showing degradation of $\rho$-, $\eta$- and $\varphi$-phase of Nd-Fe-B magnets in a hot and humid environment [86].](image)

When a metal or an alloy is immersed in an electrolyte-rich solution an electrical double layer is created at the metal/solution interface [22]. The metal side of the interface can be charged negatively or positively by providing or withdrawing electrons [22]. The charge of the metal side of the interface is balanced by a distribution of ions at the solution side of the interface.

When Nd-Fe-B magnets are placed in a saline solution a galvanic couple is created between the $\varphi$-phase on one side and the $\rho$- and $\eta$-phase on the other, with the $\rho$- and $\eta$-phase corroding first because they have the highest chemical activity (lower electrode potential). Hence, the $\varphi$-phase can be considered the cathode and the $\rho$- and $\eta$-phase the anode. Furthermore, electrochemical cells are created between the single phases and the electrolyte-rich solution, with the metal surface acting as the cathode and the solution the anode.

The pH plays a crucial role in the corrosion behaviour of these magnets. Song et al. [99] found that passivation of Nd-Fe-B magnets is in principle possible in highly alkaline solutions, because Nd-Fe-B magnets form passive hydroxide layers in sodium hydroxide solutions and in oxalic acid. In contrast, Jingwu et al. [31] observed that the
alloy freely dissolves in solutions with high current densities and is prone to attack by chloride and other ions even in those solutions in which they should exhibit passivity (eg. high pH solutions).

One of the main causes of loss of magnetic properties in Nd-Fe-B magnets is regarded to be hydrogen absorption by the φ-phase [94] and the hydrogen decrepitation and corrosion, which takes place in the Nd-Fe-B alloys, has been attributed to the formation of hydrides [100]. Only few papers have investigated the correlation between the hydrogenation process and corrosion [84] [96].

Hydrides of the pure material Nd₂Fe₁₄B were first reported by Oesterreicher & Oesterreicher [101] and then studied by others (Friedt et al. [102]). Cadogan & Coey [103] studied hydrogen absorption and desorption of multiphase technical alloys by means of thermomagnetic analysis combined with Mössbauer spectroscopy, and Wiesinger et al studied the influence of hydrogenation on the magnetic properties of Nd-Fe-B alloys. [104]. However, the amount of absorbed hydrogen reported varies considerably between studies. Rupp et al. [84] studied the effect of hydrogen absorption using X-ray diffraction techniques (using pure germanium as internal standard) and thermal desorption techniques at H pressures up to 1000 mbar. They discovered that the reaction between the Nd-Fe-B alloy and hydrogen starts at room temperature after a short incubation time (instantly to few minutes) from 10 bar on and, at 340K (66.85°C) and a pressure of around 3 bar the materials reacted completely. Rupp et al. [84] were not able to detect any significant presence of decomposition products like neodymium or iron under their experimental conditions, but were able to measure them in samples reacted at high pressures (>30 bar) and high temperatures.

Kim et al. [95] studied the effects of hydrogen induced corrosion on Nd-Fe-B magnets with magnets exposed to flowing hydrogen or exposed in a humid atmosphere at 110-115°C for 96 hours. They showed how that hydrogen- and humidity-induced corrosion progressed along the grain boundaries and was driven by the preferential local orientation of the φ-phase matrix. The samples are magnetically aligned (all the commercial grade Nd-Fe-B magnets are magnetically aligned) with the matrix grains arranged in a layered pattern and the ρ-phase also. During corrosion or decrepitation
the transformation of the ρ-phase into a hydride phase caused it to expand creating local stresses, and this effect is greatest along the continuous layers of the ρ-phase. Hence, the dishadesion of the φ-phase occurs in layers like an exfoliation process.

Hydrogen is known to enter into the Nd$_2$Fe$_{14}$B stucture [105] but high temperatures or pressures are required to initiate this reaction, and unless the rate of the exothermic reaction of the hydrogen with the Nd-rich phase is sufficient to raise the temperature to the necessary level, φ-phase absorption of hydrogen may not take place.

Yang et al. [96] studied the hydrogen uptake by a surface morphology study of charged Nd-Fe-B magnets with different cathodic current densities. They found through XRD analysis that the prominent 105 and 006 peaks of the φ-phase shift towards smaller diffraction angles, signifying an increasing cell distortion and an increasing volume of the matrix phase. This indicated that some hydrogen was incorporated into the tetrahedral interstices of the φ-phase, with the formation of hydride (Nd$_2$Fe$_{14}$BH$_x$). The hydrogen content in the hydrides was calculated to be between $x<1.04$ and $x=1.86$.

Isnard et al. [105] synthesised a pure Nd$_2$Fe$_{14}$B alloy (characterised using x-ray diffraction) and then hydrogenated it in autoclave to yield an hydride with maximum hydrogen concentration $x=5$. According to neutron diffraction and x-ray diffraction experiments the insertion of hydrogen in the Nd$_2$Fe$_{14}$B structure does not lead to a change from group symmetry P4$_2$/mnm. The main change is a massive increase in the unit-cell volume (max. 8.1 Å$^3$), with a lattice expansion found to be in the order of 2.7Å$^3$ per hydrogen atom up to three hydrogen atoms per formula unit. For higher hydrogen contents, the expansion is slightly lower, around 2.2 Å$^3$. Isnard et al. [105] noted that neither metallic Fe nor B absorb hydrogen, and also that no hydrogen atom is expected around the location of B atoms in the Nd$_2$Fe$_{14}$B structure. This is confirmed by the fact that no H atom is found in the σ-type layer that contains only Fe atoms [81] [106]. Furthermore, no hydrogen is accomodated in the tetrahedra formed by Fe and B atoms [105]. The very high electronegativity difference between the rare earth elements and hydrogen causes the insertion of H in the neighbourhood of the polyhedrons occupied by Nd.
2.3 Permanent SmCo magnets
Sintered Samarium Cobalt magnets (SmCo) were the first of the Rare-Earth permanent-magnet family. They were first developed in the 1960’s and revolutionised magnetic design by offering substantial improvements in energy product to that of other synthetic magnets such as AlNiCo and ceramic ferrites. RE$_2$TM$_{17}$ (Rare-Earth Element and Transition Metal) type magnets originated from the investigation of R$_2$(Co,Fe)$_{17}$ alloys in 1972 [107].

Attempts to develop high intrinsic coercivity in these stoichiometric permanent magnets over the subsequent years were unsuccessful, so attention was focused on Sm(Co$_{0.85}$Cu$_{0.15}$)$_{6.8}$ in 1975 and Sm(Co$_{0.85}$Fe$_{0.05}$Cu$_{0.10}$)$_{8}$ in 1976 [108]. A new alloy with formula Sm(Co$_{0.68}$Fe$_{0.28}$Cu$_{0.10}$Zr$_{0.01}$)$_{7.4}$ with $H_c$ 30MGOe was produced in 1976.

Commercial SmCo magnets have a standard formula Sm$_{2}$(Co,Fe,Cu,Zr)$_{17}$ but they are divided into two grades. The “standard” one has this chemical formula Sm(Co$_{0.65}$Fe$_{0.27}$Cu$_{0.08}$Zr$_{0.02}$)$_{8.35}$, whereas the “high-temperature” grade has a formula Sm(Co$_{0.74}$Fe$_{0.1}$Cu$_{0.12}$Zr$_{0.04}$) [109].

Sintered SmCo magnets (SmCo26 “standard” grade produced by e-magnetsUK have been used in this project) are produced by sintering a powder at a temperature up to 1250°C and then letting them cool down under the presence of an external magnetic field to produce an anisotropic magnet. They have a maximum operating temperature of 350°C, a very high resistance to demagnetization, and offer the highest energy product (BH$_{\text{max}}$), ranging from 22MGOe to 32 MGOe.

The microstructure of the Sm$_2$Co$_{17}$ alloys has been extensively characterised by several authors [110] [108] [111]. It consists of Sm$_2$Co$_{17}$ cells of the order of 100 nm in size surrounded by boundaries of SmCo$_5$, and penetrated by thin Zr-rich lamellae perpendicular to the c-axis. On a larger scale, this structure is divided into equigranular grains approximately 40-50 µm across and interspersed with 2-5 µm particles of Sm oxide formed during alloy production [109]. The hard magnetic properties in these alloys are attributed to the development of a fine scale cellular precipitate microstructure achieved through a multi-stage heat-treatment procedure, sintering and solution treatment (1433K-1483K) and isothermal aging (1073-1173K) followed by slow cooling to 673K [111]. Gopalan et al. [111] and other authors reported that the
high coercivity properties of the Sm$_2$Co$_{17}$ magnets arise from the essential formation of a TbCu$_7$-type (1:7 H) structure during the solution treatment stage and this because the anisotropy of the 1:7 H structure is greater than that of a Th$_2$Zn$_{17}$-type (2:17 R) structure.

Huang et al. [112] investigated the magnetic (with VSM and SQUID magnetometers) and crystal-chemical properties (with X-ray powder diffraction (CuKα radiation) and SEM) of several as-cast alloys of SmCo$_{7-x}$Zr$_x$, finding a direct correlation between the crystallographical changes and the Zr content x.

The XRPD traces in Figure 2-6 show a clear change in peak intensities and positions with Zr content (x). A typical superlattice line for the Th$_2$Zn$_{17}$-type (2:17 R) structure (015 + 204) disappears with x rising over 0.2. This indicates how the structure of the main phase changes from rhombohedral (Th$_2$Zn$_{17}$-type) to hexagonal (TbCu$_7$-type). This evidence is clearly supported by thermomagnetic analysis (TMA), in which the sample with x=0 shows two Curie temperatures $T_{C1}$≈920°C for the 2:17 phase (Th$_2$Zn$_{14}$-type) and $T_{C2}$≈780°C for the 1:7 phase (TbCu$_7$-type), whereas the sample
with x=0.2 shows only one Curie temperature for the 1:7 phase (TbCu$_7$-type) $T_{C2}$≈760$^\circ$C.

2.3.1 SmCo alloy corrosion in humid or aqueous media
There are no extensive studies on the oxidation of SmCo magnets in humid or wet environments, but some papers have been published on the oxidation morphology and kinetics under high temperatures (> 300$^\circ$C) [113] [109].

Pragnell et al. [109] heated two grades of SmCo magnets (one standard grade and one “high temperature” grade) at temperatures between 300 and 600$^\circ$C, for up to 1000 hours at the lower temperatures and up to 350 hours for the highest temperatures.

Both SmCo grades exhibited two main oxidation processes. A thin oxide scale formed on the exterior surface of the alloy and an internal reaction zone was found to grow into the substrate; the external oxide layer was highly adherent with no tendency to spall and a thickness of no more than 10-15µm after 300 hours at 600$^\circ$C. Based on the EDX element mapping in conjunction with XRD measurements the outermost oxide was found to be CuO, with a thin layer of Co$_3$O$_4$ just below it. The thickest corrosion-produced layer, just above the underlying alloy, was CoFe$_2$O$_4$. The oxides appeared to be layered in order of their thermodynamic stability (i.e. CuO/Co$_3$O$_4$/CoFe$_2$O$_4$) [109].

2.4 Permanent AlNiCo magnets
Alnico is an alloy containing Aluminium (Al), Nickel (Ni), Cobalt (Co) hence its name Alnico. Nevertheless, Alnico actually contains more than just these three elements. It also contains Iron and Copper with some versions also containing Titanium and even Niobium (the Titanium versions were sometimes called Ticonal, derived from the elements TiCoNiAl). Alnico magnets were developed in the 1930’s and were the first “Real” performance permanent magnets (the first “magnets”, called magnetic steels, were quickly replaced by the vastly superior Alnico).

McCaig [114] used the term Al-Ni-Co to describe all permanent magnets based on the Al-Ni-Fe system; in the UK the name AlNiCo without the hyphens is used only for isotropic alloys, containing about 12% of Co.

The composition of AlNiCo alloys is typically 8–12% Al, 15–26% Ni, 5–24% Co, up to 6% Cu, up to 1% Ti, and the balance is Fe. The commercial grade AlNiCo magnets
have these main elements percentages by weight: Aluminium 6-13%, Nickel 13-26%, Cobalt 0-42%, Copper 2-6%, Titanium 0-9%, Niobium 0-3% and balancing Iron (30-40%) (Source: http://www.alnico-info.com).

AlNiCo5 grade LNG37 magnets have been used in this study. This LNG37 is an anisotropic cast AlNiCo magnet (ACA), and is produced by pouring the molten AlNiCo alloy into sand moulds and cooling this down quickly and finally heat-treating the material under the presence of an external magnetic field to remove any unwanted second phase and give it the final desired magnetic properties (source: http://www.alnico-info.com).

Heidenreich et al. [115] found that heat-treatment produces a precipitate of aligned Co-rich face-centered cubic micro-rods (magnetically active) in a fine-grained matrix. Campbell & Julien [116] found that AlNiCo5 have a microscopic dual structure in which the precipitate and the matrix are, within experimental error, identical in lattice parameter and orientation, concluding that the precipitate/matrix structure corresponds to a miscibility gap separation within essentially crystallographically continuous volumes. Nesbitt & Williams [117], analysing torque curves of a non-heated single crystal in a magnetic field discovered that the torque decreases with increasing field. They related this unusual behaviour to the shape anisotropy of the precipitate; hence, they suggested that the coercive field of AlNiCo 5 is due to the shape anisotropy of the precipitate and not to the crystalline anisotropy.

2.5 Permanent Ferrite magnets
Ceramic magnets became commercially available in the 1950’s. They are called ceramic magnets because of their electrically insulating properties and their production method. They are better known as Ferrite permanent magnets but their correct title should be hard hexagonal ferrite permanent magnets.

Ferrite magnets have ferrimagnetic properties. Compared to AlNiCo, ferrite has much higher intrinsic coercivity making it much better at resisting demagnetisation from external magnetic fields and from other magnets. This has enabled it to be used much more successfully in electric motors and generators where it is still an extremely popular magnet. The hexagonal ferrite structure is found in both $\text{Ba}_{0.6}\text{Fe}_2\text{O}_3$ and
Sr$_{0.6}$Fe$_2$O$_3$ (the chemical symbols for each type of ferrite), but the strontium (Sr) version of ceramic ferrite magnet has stronger magnetic properties.

Ceramic ferrite magnets are often very low cost, due to the ease of processing and the low cost of raw materials. As a result, they are one of the most widely used permanent magnet materials in the world. Ferrite Magnets are produced by calcining (between 1000 to 1350 degrees C) a mixture of iron oxide (Fe$_2$O$_3$) and strontium carbonate (SrCO$_3$) or barium carbonate (BaCO$_3$) to form a metallic oxide (http://www.ferrite-info.com/).

The main production method involves mixing the fine powder with water to produce a slurry which is then compacted in a die in the presence of an externally applied magnetic field. The external magnetic field helps the hexagonal crystal structure align more perfectly with the magnetic field, improving the magnetic performance. This results in an anisotropic ferrite magnet with stronger magnetic properties but it will possibly require additional machining stages to give the final dimensions. The compacted magnets are then sintered (at a temperature between 1100-1300 degrees C) to fuse the particles together (http://www.ferrite-info.com/).

There are no problems with oxidation of the powder during processing, as the material is already a stable oxide. The powder processing route ensures that the magnets are comprised of very small grains (<1mm), which is essential for generating coercivity in these magnets. During processing, the powder is compacted in a magnetic field in order to align the easy direction of magnetisation of the particles and hence enhances the remanence and the maximum energy product.

### 2.6 Magnetite

Magnetite is a natural magnetic mineral belonging to the spinel group, and is the main ore mineral for iron. It belongs to the isometric crystal system and has a chemical formula Fe$_3$O$_4$ and crystallographic formula (Fe$^{3+}$)$_8$[(Fe$^{3+}$)$_8$ (Fe$^{2+}$)$_8$]O$_{32}$.

The unit crystal cell of a spinel is conventionally made up of eight flanked cells, so the chemical formula AB$_2$O$_4$ becomes the structural formula A$_8$B$_{16}$O$_{32}$. The unit cell of spinel is cubic face-centered (space group $Fd3m$) and, if it is seen along the cell diagonal, features alternate planes of cations and anions, so these can receive electric
charges from both the 4-coordinated cations and the 6-coordinate cations. Magnetite has a fully inverse spinel-type structure, with a face-centered cubic cell with anions packed according to a cubic close-packed array along the crystallographic plane (111). Octahedral sites share 1 or 2 edges with other octahedra and four vertices with tetrahedrons. The unit cell length is \( a = 0.839 \) nm.

Magnetite is unstable under the pH conditions generally measured in standard groundwater compositions, and those are assumed to be the initial water conditions in a Geological Disposal Facility.

Swaddle & Oltmann [118] have reported that coarsely grained magnetite (>20 \( \mu \)m) undergoes slow oxidation to hematite, whereas fine-grained magnetite (<10 \( \mu \)m) is transformed rapidly to maghemite. The smaller the grain size, the faster the oxidation.

Temperature also affects both the kinetics and the final product, because at ambient temperatures (15-20\(^\circ\)C) the transformation is kinetically controlled, and magnetite oxidation produces maghemite through a topotactic reaction. At higher temperatures (>200\(^\circ\)C) maghemite decomposes in oxidative conditions to hematite.

In the dry state, magnetite is readily oxidized to maghemite by air. Ultrafine (<100 nm) crystals of magnetite change over years from black to the brown of maghemite even at room temperature [119]. Under those conditions, the oxidation of magnetite involves a topotactic reaction in which the original crystal morphology is maintained throughout.

Sidhu et al. [120] compared the oxidation upon heating of natural and synthetic magnetites, finding that natural magnetites were more resistant to oxidation, and higher temperatures or longer times were needed for oxidation to take place.

In water or alkaline solutions under hydrothermal conditions, magnetite transforms to maghemite and thence to hematite. The conversion to maghemite implies outward migration of cations via cation vacancies [118]. The hydrothermal transformation is slower than that in air at the same temperature (180\(^\circ\)C), and it has been suggested that this is because the cation vacancies which assist cation diffusion are reduced or eliminated by the large excess of water.
The following topotactical reaction is considered to govern the reaction of magnetite to maghemite:

\[
(\text{Fe}^{3+})_8[(\text{Fe}^{2+})_8(\text{Fe}^{3+})_8]\text{O}_{32} \rightarrow (8\text{Fe}^{3+})_A[40/3\text{Fe}^{3+} + 8/3\Delta]_B\text{O}^{2-}_{32}
\]

\textit{Magnetite} \quad \textit{Maghemite}

This reaction causes a complete rearrangement of the cationic positions, leaving the anionic array unaltered. In fact, maghemite is an oxide with a spinel-type structure that does not have all of its octahedral positions filled.

The spinel cell is conventionally formed by eight flanked cells to form a large cube, so every cell has 32 tetrahedral positions and 64 octahedral positions. In magnetite and maghemite, only 8 tetrahedral positions on 32 are occupied but something changes in the octahedral positions. Only 16 octahedral positions (8 by ferrous ion and 8 by ferric ion) of the 64 are filled in the magnetite crystal structure.

In the maghemite crystal structure ferrous ions are not present so, to maintain the electric balance (for the second Pauling rule), some structural vacancies in the octahedral sites must be present in order to maintain the inverse spinel type structure. This has important implications for the magnetic structure of maghemite and especially on the balance of the charges.

During oxidation of magnetite, initially a mixed phase, \(\text{Fe}^{2+1-x}\text{Fe}^{3+2+x}\text{O}_{4+0.5x}\), with less \(\text{Fe}^{2+}\), more \(\text{Fe}^{3+}\) and more cation vacancies than magnetite, forms. This phase then oxidizes further [121]. During the reaction, the density of the starting material decreases and the total weight of the material increases because oxygen is taken up: \(4\text{Fe}_2\text{O}_3 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3\).

No porosity develops, however, and the sample surface area does not change [122]. Oxidation to maghemite involves a reduction in the number of Fe atoms per unit cell of 32 oxygen ions, from 24 in magnetite to \(21 \frac{1}{3}\) in maghemite.

The reaction proceeds by outward migration of the cations towards the surface of the crystal together with the creation of cation vacancies [123] [124] and the addition of oxygen atoms. At the surface the cations are oxidized and interact with adsorbed oxygen to form a rim of maghemite. The diffusion coefficient for cation migration is

74
1-2x10^{-15} \text{ cm}^2/\text{s} [125]. Activation energies for this transformation are between 83.6 kJ/mol [122] and 137 kJ/mol [126].

The grain-size dependence of magnetic properties was first investigated by Parry [127] on dispersed magnetite powders and then by Day et al. [128], who published a breakthrough paper establishing the single-domain/multi-domain transition in fine grained magnetic materials to determine the magnetic behaviour in the size range of the transition. Day et al. [128] concluded that the coarse-grained (soft) samples did not show compositional dependence and the magnetic behaviour of those grains was essentially that of multi-domain grains, whereas the fine-grained (hard) samples showed compositional dependence and the magnetic behaviour of single domain grains.

Studying mixtures of soft and hard material, they discovered how in a mixture with less than 20% of the hard fraction coercivity was dominated by the soft fraction whereas remanent coercivity and remanence increased systematically with increasing amount of hard fraction. In the samples with 50% or more of hard fraction, the remanent coercivity is dominated by the hard fraction and is constant, while the coercivity decreases systematically with the amount of soft material present [128]. The transition from Single-Domain to true Multi-Domain behaviour is not sharp but there is a transition area (called Pseudo-Single-Domain). One of the methods used first by Day et al. [128] and then by Dunlop [129] was a graphical approach (Figure 2-7) based on two or more magnetic properties. In particular, a diagram plotting Mrs/Ms (remanence vs. saturation remanence) against Hcr/Hc (coercivity of remanence vs. coercivity) showed a definite trend from multi-domain grains to single-domain, with most of them falling in the transitional region [128].
Day et al. fix the limits between Pseudo Single Domain and Multi Domain at 0.05 for Mrs/Ms and at 4 for Hcr/Hc. Day et al. found that the calculated Single Domain critical size (transition to Multi Domain) for titanomagnetites depended on the compositional parameter x and on crystal elongation and varied between 0.08 and 0.26 μm, but experimentally between 0.1 and 2 μm. In general, titanomagnetite multi-domain grains are characterised by Mrs/Ms ~ 0.05 and Hcr/Hc ~ 5. The upper limit of the transitional Pseudo Single Domain area was fixed at Mrs/Ms = 0.5 after theoretical calculations.

Figure 2-7: Graphical approach using Mrs/Ms vs. Hcr/Hc with limits drawn after [129]. Day et al. fix the limits between Pseudo Single Domain and Multi Domain at 0.05 for Mrs/Ms and at 4 for Hcr/Hc [128]. Day et al. found that the calculated Single Domain critical size (transition to Multi Domain) for titanomagnetites depended on the compositional parameter x and on crystal elongation and varied between 0.08 and 0.26 μm, but experimentally between 0.1 and 2 μm. In general, titanomagnetite multi-domain grains are characterised by Mrs/Ms ~ 0.05 and Hcr/Hc ~ 5. The upper limit of the transitional Pseudo Single Domain area was fixed at Mrs/Ms = 0.5 after theoretical calculations.
3 Experimental and analytical methodologies

This chapter will explain in detail the preparation of the materials for the experiments, the experimental set-up and the analytical techniques used, highlighting problems encountered throughout the project and the solutions adopted to overcome them.

3.1 Experimental methodologies

3.1.1 Preparation of clay

The clay sample (industrial grade MX80 Na-bentonite from Wyoming, USA) was supplied by RS minerals and ClayTechAB in doughnut discs weighting 15 kg each with dry density of 1700 kg/m$^3$ and a moisture content of 11%. Since we were not interested in measuring engineering parameters such as lateral/vertical swelling pressure and water suction, we decided to use powdered clay instead of cylinders of compacted material, which would have required more complex and expensive experimental set-ups, limiting the number of replicates that could be performed. The block of clay was trimmed using a sharp kitchen peeler and then the trimmings powderized either using an agate mortar or a TEMA Ltd. Laboratory Disc Mill pouring material into a holder containing tungsten carbide discs. The agate mortar method, despite being more time consuming than the automatic powderized, allowed recovery of almost all the material. The powders were not sieved to produce a homogeneous grain size distribution.

3.1.2 Preparation of magnetite

Pure magnetite ore was supplied by Dr. Henrikki Rutanen (Senior mine geologist for Luossavaara-Kirunavaara AB, Kiruna, Sweden) and the material was first crushed using a sledgehammer and a jaw crusher, then powderized using the TEMA Ltd. Laboratory Disc Mill with tungsten carbide discs. I had prepared three sets of magnetite samples, based on grain size

1. Bulk crushed sample (code Kirmag0.5 or b). It was pulverized for 30 seconds and neither sieved nor cleaned from the magnetite powder.

2. Grain size greater than 120 μm (code c). This material was separated directly from the bulk-crushed sample using a sieve with mesh 120 μm and then cleaned. Dust was removed from the sieved material using a standard desk vacuum cleaner with a plastic fabric mesh (10 μm) taped to the vacuum cleaner.
nozzle. The material was then repeatedly stirred and gently rubbed with the nozzle.

3. Magnetite powder (code a). This material was run in the Laboratory Disc Mill for 2 minutes, and then sieved using the smallest mesh available (10 μm).

### 3.1.3 Preparation of synthetic magnets

Commercially available synthetic magnets Nd-Fe-B (grade N42) and SmCo (grade SmCo26) were supplied by Emagnets UK, whereas AlNiCo (grade AlNiCo5) and Ferrite (grade F30) were supplied by ENES magnets. Since the batch experiments were primarily focused on the identification of the main candidates for the following long-term experiments, the original block magnets were broken and fragmented using a sledgehammer and then weighted. The Nd-Fe-B magnets were purchased coated with a NiCuNi triple coating, which was removed before fragmentation using a sandblaster.

For the long-term experiments, small cylinders of the same magnet grades used in the batch experiments were used (Table 3-1). The uncoated Nd-Fe-B magnets were initially long coated cylinders, which have been first uncoated then cut to make smaller cylinders. All alloy cylinders are magnetised along the z-axis.

<table>
<thead>
<tr>
<th></th>
<th>Coated</th>
<th>Grade</th>
<th>Diameter</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd-Fe-B</td>
<td>Yes (NiCuNi)</td>
<td>N42</td>
<td>3mm</td>
<td>2mm</td>
</tr>
<tr>
<td>Nd-Fe-B</td>
<td>No</td>
<td>N42</td>
<td>3mm</td>
<td>4mm</td>
</tr>
<tr>
<td>SmCo</td>
<td>No</td>
<td>SmCo26</td>
<td>3mm</td>
<td>1mm</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>No</td>
<td>AlNiCo5</td>
<td>4mm</td>
<td>4mm</td>
</tr>
</tbody>
</table>

*Table 3-1: synthetic magnets used in the long-term experiments. The differences in the dimensions are due to the availability of stocks and the impossibility of obtaining custom made magnets in small lots.*

### 3.2 Preparation of samples for the batch experiments

#### 3.2.1 Magnetite/bentonite samples and control samples (BM series)

The samples belonging to the BM (bentonite and magnetite) series were prepared in tightly sealed 50 mL glass Serum bottles. Bottles were filled to 75% by volume (37.5 mL) by a mixture of bentonite and magnetite (11.25 mL) and an aqueous solution (26.25 mL).

A void space (25%, or 12.5 mL) was left at the top of the Serum bottle to account for bentonite swelling and prevent excessive pressure within the bottle.
The bentonite/magnetite mixtures that had been prepared consisted of 11.25 mL of bentonite (10.68 grams) and 0.56 mL of magnetite (2.89 grams) in volume.

The solutions used in the batch experiments are listed in Table 3-2.

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
<th>Molar conc.</th>
<th>Grams of solute</th>
<th>pH</th>
<th>Usage number</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>Deionized H₂O</td>
<td></td>
<td></td>
<td>6.5</td>
<td>3</td>
</tr>
<tr>
<td>W2</td>
<td>H₂O + NaCl</td>
<td>1M</td>
<td>14.659</td>
<td>6.5</td>
<td>3</td>
</tr>
<tr>
<td>W3</td>
<td>H₂O + NaOH</td>
<td>0.1M</td>
<td>1.04</td>
<td>11.95</td>
<td>3</td>
</tr>
<tr>
<td>W4</td>
<td>H₂O + KOH</td>
<td>0.1M</td>
<td>1.408</td>
<td>12.25</td>
<td>3</td>
</tr>
<tr>
<td>W5</td>
<td>H₂O + Ca(OH)₂</td>
<td>0.05M</td>
<td>0.764</td>
<td>11.97</td>
<td>3</td>
</tr>
<tr>
<td>W6</td>
<td>H₂O+NaCl+KCl+CaCl₂ +NaOH+KOH+Ca(OH)₂</td>
<td>0.5M salts</td>
<td>12.85</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>W7</td>
<td>H₂O + KCl</td>
<td>1M</td>
<td>18.637</td>
<td>6.5</td>
<td>3</td>
</tr>
<tr>
<td>W8</td>
<td>H₂O + CaCl₂</td>
<td>1M</td>
<td>27.74</td>
<td>6.5</td>
<td>3</td>
</tr>
</tbody>
</table>

*Table 3-2: Composition of the solutions used in the batch experiments with pH values.*

The samples then have two different arrangements of these bentonite-magnetite mixtures (Table 3-3).

**BMα:** Uncompressed magnetite and bentonite (to evaluate mineral alteration and variation of magnetic signal with free water uptake and reaction). Powdered bentonite density was 0.8 gr/cm³.

**BMβ:** Compressed pills of mixed bentonite and magnetite (to evaluate mineral alteration and variation of magnetic properties during clay swelling and with water uptake controlled by the swelling of compressed bentonite). Bentonite density was 1.6-1.7 gr/cm³.

The cylindrical pills of compressed BM mixture (β-configuration) were produced in a pin press with a load of 512-650 kg on a surface of 50.24 mm² (8mm diameter) for a total pressure between 100 and 120 MPa. The pills had a length between 1.7 and 2.5 cm for a total volume of 1004.8 mm³ (8 mm).

In order to obtain control data on magnetite and bentonite reacted separately in solution, the solids were reacted with the same waters as used in mixed experiments in tightly sealed serum bottles (15 mL volume) with the same solid/liquid ratio used in the mixtures (Table 3-3).
Table 3.3: List of samples of the batch experiments using magnetite. In blue are presented the control samples (magnetite only) and in green the samples of the bentonite-magnetite mixtures. a: magnetite powder (<10 μm), b: bulk crushed magnetite, c: grain size > 120 μm. W1-8 refers to solution composition in Table 3-2. MT magnetite-only, BM bentonite/magnetite

3.2.2 Synthetic magnets/bentonite samples

In these samples the crushed magnets were mixed with bentonite with the same volumetric proportions as described in the previous section. Some of the samples were reacted in larger bottles and some in smaller depending on the quantity of magnets that was available.

Table 3-4: List of the samples of batch experiments using the synthetic magnets embedded in bentonite (NdFeB+bentonite, AlNiCo+bentonite, SmCo+bentonite and Ferrite+bentonite sets). W1-8 refers to solution composition in Table 3-2.
For the solution compositions and pH refer to Table 3-2; in Table 3-4 all samples are listed with its relative solutions. As a result of the very high magnetic field of these magnets, the various grains of the starting materials clumped together during the pouring of the mixture in the glass vessels, forming agglomerates dispersed in the sample.

The synthetic magnets were also tested with solutions without bentonite (Table 3-5) in order to provide control data.

<table>
<thead>
<tr>
<th></th>
<th>NdFeB-only set (Nd-only)</th>
<th>AlNiCo-only set (Al-only)</th>
<th>SmCo-only set (Sm-only)</th>
<th>Ferrite-only set (Fe-only)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W2</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W3</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W4</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W5</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W7</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td>W8</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
<td>1 (30mL)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total 28</td>
</tr>
</tbody>
</table>

Table 3-5: List of the synthetic magnets control samples of batch experiments (NdFeB-only, AlNiCo-only, SmCo-only and Ferrite-only sets). W1-8 refers to solution composition in Table 3-2.

3.3 Set-up of the long-term experiments in confined fluid flow regime

The aim of this set of experiments is to evaluate the corrosion behaviour of the synthetic magnets under confined fluid flow in low dissolved oxygen conditions typical of subsurface environments. In contrast to the batch experiments, in which the pH of the solution was free to drift and there was no continuous supply of reactants, in this experiment the aim was to maintain a continuous supply of reactants from reactant solution and to react the magnets in a dysoxic environment with advective reactant recharge. This design enables simulation of the time-dependent evolution of repository conditions such as:

- Groundwater influenced by an alkaline plume generated by the reaction of cementitious grout
- Diffusive movement of solution within the bentonite backfill
- Local transport of metal cations speciated in solution
Fe-bentonite interaction under anaerobic conditions

The design consisted of three stacks (Figure 3-1) of reaction vessels (Table 3-6).

<table>
<thead>
<tr>
<th>Stack</th>
<th>Duration</th>
<th>Number of vessels</th>
<th>Composition vessel1</th>
<th>Composition vessel2</th>
<th>Composition vessel3</th>
<th>Composition vessel4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack 1</td>
<td>12 months</td>
<td>4</td>
<td>BT/ Nd-Fe-B coated</td>
<td>BT/uncoated Nd-Fe-B</td>
<td>BT/SmCo</td>
<td>BT/AlNiCo</td>
</tr>
<tr>
<td>Stack 2</td>
<td>12 months</td>
<td>1</td>
<td>Bentonite only</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Stack 3a</td>
<td>4 months</td>
<td>4</td>
<td>BT/ Nd-Fe-B coated</td>
<td>BT/uncoated Nd-Fe-B</td>
<td>BT/SmCo</td>
<td>BT/AlNiCo</td>
</tr>
<tr>
<td>Stack 3b</td>
<td>8 months</td>
<td>4</td>
<td>BT/ Nd-Fe-B coated</td>
<td>BT/uncoated Nd-Fe-B</td>
<td>BT/SmCo</td>
<td>BT/AlNiCo</td>
</tr>
</tbody>
</table>

Table 3-6: List of stacks used in the long-term experiments.

Stack 3a was placed in the oven along with stack 1 and 2 (Figure 3-3), and then extracted and substituted by stack 3b after 4 months. Stack 3b was finally extracted with stacks 1 and 2 after a further 8 months. This allowed us to reconstruct alteration pathways and analyse the variation of the magnetic properties through time using samples distributed along a regular timeline. The extraction of Stack 3A after 4 months allowed a comparison with the samples from the batch experiments in order to assess if the behaviour under dysoxic conditions followed the same trends observed for those batch experiments samples.

Each of the three aqueous reactant reservoirs (2L media bottles) was filled with the same solution composition (0.5 * seawater NaCl concentration) and mass (234 grams) of ground cement (to form a layer of approximately 1.5 cm at the bottom of the tank) (Figure 3-2). The pH of the resultant solution was comprised between 11.9 and 12.3.

The cement used in the experiment was an aged NRVB (Nirex Reference Vault Backfill) cement kindly supplied by Dr. J. Butcher (National Nuclear Laboratory). The composition and preparation technique, as well as the chemical properties of the material, are described elsewhere [130].

Each reservoir had one water inlet and outlet and one N₂ gas inlet and outlet respectively. The water outlet tubing (1/16” ID-1/8”OD FEP (Fluorinated Ethylene Propylene) tubing) was located exactly at half height of the bottle, whereas the inlet tubing was located at the bottom of the bottle, in order to guarantee circulation of water within the grout and hence ensure water reaction with the solid.
Figure 3.1: Schematic representation of a cross-section of a reaction vessel and of a complete stack of reaction vessels (Stack 2, 3A or 3B). The black arrows indicate the direction of the advective flow, whereas the blue waves indicate the diffusive flow within the bentonite. This design has the virtue of maintaining a buffered pH and total reactant concentrations, whereas the blue waves indicate the diffusive flow within the bentonite. The bentonite matrix is intended as a low porosity buffer that minimizes the movement of metal ions in the system. The interaction between the vessels is minimal because any eventual dissolved material entering the advective system would be so diluted to have no effect on the stability of the chemistry of the following vessel.

- a: Lid
- b: Reaction vessel
- c: Porous sintered glass disc
- d: Bentonite
- e: Permanent magnets cylinders
- f: Groove for the O-ring
- g: Solution inlet
- h: Solution outlet

The arrows describe the direction of the advective flow of the solution. The blue wavy lines the diffusive flow within the bentonite layer.
Water outlet tubing (L/S 14 Norprene©) was then connected to a dual-head Masterflex Console Drive (Peristaltic Pump). The tubing serving stack 1 and 2 were set on the first head, the one serving stacks 3a and 3b on the second head. Before entering in the oven, the flexible peristaltic pump tubing was changed into FEP tubing.

The reservoirs were purged with oxygen-free nitrogen gas (N₂) that was saturated with water in a Dreschel bottle before being bubbled in the reservoirs. At the very beginning of the experiment, the gas flow was increased to sparge the oxygen out of the reservoirs quickly and then reduced to a minimum low to maintain low oxygen conditions and conserve gas. The gas inlet was located at the bottle base, whereas the outlet was located close to the screw cap. The gas going out of the reservoirs was channelled through a water-filled beaker to eliminate back diffusion of oxygen.

The water flow was tested with and without the filters attached at the water inlets to evaluate the effects of mesh aperture on the water flow and the possibility of having cavitation effects as the peristaltic pump draws solution. The chosen flow rate was 3 mL/min, corresponding to 55 rev/min of the peristaltic pump.
In order to maintain a constant temperature of 70°C in the water circulating within the vessel stacks, the water flowing from the external, room-temperature, reservoirs was heated up at the right temperature within the oven before reaching the vessels.

*Figure 3-3: The stacks of the reaction vessels inside the oven (picture taken before the start of the experiment). Stack 2 is not visible, being behind stack 1. The heat exchange unit made of a big brass cylinder with the tubing coiled around is visible in the lower part of the picture.*

To do this, a 3” diameter cylinder of brass was used and the FEP tubing coiled around it three times. The FEP tubing was taped to the brass with a heat-resistant tape.

The reaction vessel consisted of one simple cylindrical base/lid couple made of Delrin® Acetal homopolymer (Figure 3-1 and Figure 3-4).
A sketch of a cross section of a reaction vessel and a stack of reaction vessels is visible in Figure 3-1. The basin had a thin layer of bentonite at the bottom, then the cylindrical magnets covered by another layer of bentonite (Figure 3-5). The complete burial of the magnets was extremely important because it would have increased the pathway needed to the metals-enriched interstitial waters to reach the filtering system and hence the water-flow system. This means that the magnets are encased in a diffusional transport regime, as we expect them to be within a bentonite block within or near the wall of a repository.

![Figure 3-4: Delrin® reaction vessel (1) on the top part of the picture with its lid (2) (and the two water tubing). On the bottom part the filtering system with the two smaller paper filers (3), the porous sintered glass disc (4) and the bigger paper filter (5). The paper filter was a Whatman No1 qualitative cellulose filter.](image)

In order to minimize the swelling pressure generated by the wet bentonite on the sinter glass discs several swelling tests were performed to measure the deformation of the cell along the vertical axis on the stack. The tests were performed with 20, 18 and 16 grams of bentonite powder and the pressure was measured using a dial gauge pointed at the centre of the upper plate of the clamping system. The sample containing 16 grams of bentonite did not register any deformation, hence 16 grams was the preferred bentonite mass used in the experiment.
The filtering system comprised one Whatman® No 1 filter paper (5 cm diameter) in contact with the clay and then a sintered glass disc (porosity grade 0 and thickness 0.5 cm) (Figure 3-4). The porous glass disc allowed either horizontal or vertical flow of water; this facilitated the diffusion of the solution into the reaction vessels to the whole bentonite face and not only the flow towards the water outlet.

![Image](image_url)

*Figure 3-5: The vessels were filled with an initial layer of powderized bentonite, then the magnets were disposed in a sort of face-centred pentagonal fashion (in the picture, the vessel containing AlNiCo magnets is shown), then covered by another layer of bentonite.*

The lid consisted of a cylinder with a small step at the bottom (height 5mm and 56 mm diameter) and two drill holes communicating with a threaded hole for the flangeless fitting made to host FEP 1/16” ID (1/8” OD) industrial tubing (Figure 3-1). The outlet and inlets tubing were connected through FEP tubing to prevent clogging around the connection areas and the tubing was left slightly longer than the necessary (around 5 cm) to prevent tubing collapsing as it is bent beyond its minimum bend radius.

Considering the coefficient of thermal expansion of Delrin Acetal plastic (13.5 × 10⁻⁵ m/m°C) and the dimensions of the stack (24 cm of height) the calculated vertical thermal expansion in the worst-case scenario for the whole stack was about 3.9 mm. Hence, before starting the fluid flow the cells were left in the oven for a couple of hours at a constant temperature of 70°C with the clamping system left slightly loose.
to accommodate the thermal expansion, then clamped tightly when the plastic expanded.

The clamping system was made with two circular plates of 1.2 cm thick black Acetal homopolymer sheets at both ends of the stack clamped using threaded stainless steel rods and wing nuts. The rod holes were put 90° from each other at a distance of 4 cm from the plate centre.

The tubing coming out the oven needed to be cooled down before entering the water reservoirs (the temperature of the reservoirs needs to be constant at room temperature) so they were coiled and put in a water bath with water at room temperature or slightly colder. In addition, before the water bath a system to collect water flow to perform pH measurements was inserted; consisted in a Delrin plastic threaded cylinder with two flangeless nuts at both ends. All connections were made with Upchurch ¼” 28tpi UNF flat-bottomed fittings as used for low-pressure chromatography applications.

3.3.1 Problems encountered during the confined-fluid flow experiments
The problems encountered during the Long Term Experiments in Confined-Fluid Flow regime were mainly related to two main issues:

- Tubing clogging
- Corrosion of Delrin® Acetal plastic

The clogging was found to be mainly related to the precipitation of calcite and (subsequently) halite in the solution inlets and outlets of the vessels, and sometimes in the tubing connecting the outlets of the vessels with the reservoirs. The problem was solved through cleaning of the inlets and outlets and a substitution of the clogged tubing.

The clogging sometimes caused overpressure around the flangeless fittings with consequent leaking of solution. This issue was solved with a constant monitoring and attention to the sensitive areas. A more serious problem was caused by the failure of the sealing system (Figure 3-3 and 3-4), which was caused by infiltration of Chlorine-rich solutions into the O-ring groove. This trapped solution slowly corroded the plastic, enlarging the groove and hence increasing the amount of space available for newly infiltrated solution. With the ongoing corrosion, channels (Figure 3-6) were created in
the plastic that reached the vessel wall, allowing the supply of oxygen which caused the failure of the cell. The cell unfortunately affected by this process (Stack 3B – SmCo vessel) was extracted and hence that part of the experiment aborted.

![Figure 3-6: Effects of the corrosion on the plastic lid by the Chlorine-rich solution. Between the outer walls and the lid step, the corrosion channels are visible. They reached a maximum length of 7-8 mm and a depth of 4 mm.](image)

3.4 Extraction of the samples
After the end of the experiments, batch and long term samples were sampled in slightly different ways.

3.4.1 Batch experiments
Samples containing the corroded magnets used for magnetic and XRPD analysis were cored out of the reaction vessels using a rigid plastic tubing (1cm ID) then frozen, dried and preserved in a fridge with both ends of the core sealed using Parafilm wrap.

All the samples with the synthetic magnets were subjected to water extraction to analyse the content of dissolved metals. The filtering process was carried out in order to have the purest water possible for the ICP-OES analysis, because the presence
material in suspension (especially colloidal bentonite) might negatively affect the output data.

The solution in the samples with magnets only were sampled using a 5mL pipette and then filtered using a 0.2 µm cellulose nitrate Whatman™ filter in a Swinnex® Millipore filter holder attached to a Luer-lock syringe. The same filtering procedure was used for samples from the supernatant solution in synthetic magnets/bentonite samples treated with saline solutions. Samples that did not have any water column at the end of the experiment had their interstitial solution extracted after centrifuging the clay for 1 hour at 14000 rpm; then the water was filtered as described above.

Magnetites and synthetic magnets were prepared for the XRPD analysis by pulverizing them in acetone using an agate mortar; before the pulverisation were crushed wrapped in Aluminium or Melinex® foil using a sledgehammer.

3.4.2 Long-term experiments
The reaction vessel stacks were initially disconnected from the fluid flow and then extracted and allowed to cool down overnight. After carefully removing the lid, the extraction of the sinter glass disc presented some issues mainly related to the dissolution of silica in high pH solutions and consequent reprecipitation of silica at the contact between the disc and the plastic (the initial fluid was not equilibrated with silica). The discs featured a pattern of fractures (due to the pressure exerted by the swollen bentonite), sometimes filled by halite, and had to be broken and the fragments carefully extracted using metal tweezers. The filter paper was scratched off using a plastic spatula. The clay matrix was sampled at the top and at the bottom of the vessel, in order to allow assessment of the different physical and mechanical behaviours seen between the two layers.

When the bentonite matrix showed traces of newly precipitated mineral phases (Fe-oxyhydroxides) these volumes were sliced using a scalpel and stored. Magnets were handpicked using tweezers (if the magnet was not disaggregated) or cored out using rigid plastic tubing. Either clays or magnets were freeze-dried and then stored in a fridge.
3.5 Analytical methodologies

3.5.1 XRPD analysis
XRPD analysis were performed in the XRD laboratory at the Grant Institute of Geosciences under the supervision of Dr. Nicholas Odling using a Bruker D8 Advance diffractometer with Sol-X Energy dispersive detector. Lists of analysis can be found in electronic appendix 3.5.1. for the batch experiments and appendix 3.5.2 for the confined-fluid flow experiments.

3.5.1.1 Clay samples
Characterisation of the original starting clay sample was made using a random powder and oriented sample.

**Starting material**
The original starting material MX80 sodium bentonite was subjected to separation of the fine clay material from the accessory minerals through dispersion of a homogenized sample in deionized water and ultrasonic bath for 6 minutes; the suspended material was left to decant for 40 minutes for each cm of water column and then the supernatant collected with a pipette. The operation was repeated until the supernatant was clear and the precipitated material was clay-free.

Scan parameters were: scan range 2-70°2θ, step size 0.02° and step time 2 seconds.

**Batch Experiments**
The clays were sampled at the magnet/matrix interface, being removed using a tiny spatula. After that the material was put in a glass vessel with a block magnet underneath, some acetone was added and the slurry stirred or put in an ultrasonic bath for two minutes in order to separate the clay from any dispersed magnetic phases. Acetone was used instead of deionised water to prevent further oxidation of the magnets.

In the case of the magnetite/bentonite mixtures the material separation was made by stirring the material in acetone within an ultrasonic bath with a block magnet underneath, sucking up the clay slurry with a plastic pipette until the magnetite grains were perfectly clean.
The samples which contained newly precipitated material were treated to iron oxide removal using sodium dithionite citrate system buffered with sodium bicarbonate; the followed procedure is explained in detail elsewhere [131].

XRPD analysis on the oriented mounts of the batch experiments was performed following the guidelines given by Moore and Reynolds [34]:

- The first analysis was of air-dried samples.
- The second analysis was of glycolated samples (the samples were suspended over Ethylene-Glycol and heated in an oven at 60⁰C for minimum four hours and then analysed sequentially to prevent evaporation of the ethylene-glycol and substitution with water).
- The third analysis was of 400⁰C-heated samples (left in a furnace for one hour at 400⁰C).
- The fourth analysis was of 550⁰C-heated samples (left in a furnace for one hour at 550⁰C).

The scan parameters for the oriented mounts of the batch experiments were 2-70⁰ 20 range with 0.025 step size and 1.5 sec step time or 2-40⁰ 20 range with 0.025 step size and 1.5 sec step time for the clays subjected to Fe removal.

After data collection the traces were processed using Bruker DIFFRAC.EVA software (for plotting data on excel datasheets). The steps comprised:

1. Background removal: removes the effect of the background signal, giving a flatter XRPD profile. This used an enhanced automatic background removal function, which gives a smooth curve where some peaks may be under the background curve.
2. Kα₂ stripping: uses the Rachinger method in its classic form, or in a dynamic modification that optimizes the adjustment of the distribution functions of the profiles that are Kα₂-stripped in succession during the 2θ scanning [132].
3. Trace smoothing: uses the Savitzky-Golay method [133] to give better-defined peaks and eliminate noise.
4. Search by number, matching and merging: this is the first step for the calibration. If recognizable peaks of other phases are present, the relative PDF
(Powder Diffraction File) files are selected and merged with the height of the scanned profile.

5. Displacement: the peaks are moved in order to calibrate them with the position of the peaks of the PDFs profiles.

The calibration of the clay samples required particular attention especially for the noisy traces; some of the peaks were not well defined or narrow and so were calibrated using a highest peak approach.

The calibration was performed using different internal calibration standards; the 101 quartz reflection at ca. 26.6°2θ (PDF00-046-1045) and the halite reflections at 31.74°, 45.48° and 56.48°2θ (PDF00-005-0268) were used.

**Confined-Fluid Flow experiments**

For the long-term experiments, more precise analysis were performed because clay/cement porewater interaction is a subject of increasing scientific interest and hence a more detailed analysis of the peaks was required.

For the oriented mounts, the clay fraction was separated from the accessory phases using the same methodology as used for the characterisation of the raw material. An oriented mount for the clay fraction and one random mount for the accessory phases were prepared. The clay fraction was not treated with either fluoridric acid or hydrocloric acid, which would generally be used to eliminate quartz and calcite respectively, so as not to cause any change in the mineralogy of the reacted bentonite.

Scan parameters were changed from batch experiments samples: scan range 2-70°2θ, step size 0.02° and step time 2 seconds. In addition, a scan on non-separated random oriented powders was run using the same scan parameters but step size 0.01°.

Randomly oriented powder mounts have been prepared by hand-milling in an agate mortar a known mixture (in weight %) of sample and an internal standard (analytical grade zincite ZnO [134]). The amount of zincite in the sample was fixed at 10% following Srodón et al. [134]. Spray drying to guarantee maximum homogeneity of the sample and prevent orientation of clay particles [135] was not possible for the tiny amount of material available and given the high loss of material during the operation.
Hence, the material was disposed on a mount to form a flat surface and tapped to guarantee the maximum possible random disposition of clay platelets.

The XRPD traces were plotted without processing the higher-resolution scans.

### 3.5.1.2 Magnetite samples
Pulverized magnetite samples were deposited on a glass slide, flattened using a thicker glass slide, and then analysed in the range 25-45° 20 with 0.01 step size and 2 sec step time. As an internal standard, pure reagent grade NaCl was used.

### 3.5.1.3 Neodymium magnets
Nd-Fe-B alloy was initially characterised using a broad 2θ range (2-90°2θ, 0.025 step size and 1 sec step time) then, after comparison with traces in the literature, a smaller and more detailed scan was chosen (22-85°2θ, 0.012 step size and 2 sec step time). Reagent grade pure germanium (99.999%) was used [84] as internal standard.

Analysis with DIFFRAC.EVA allowed evaluation of the deviation in °2θ of the main reflections from the raw unreacted material and the reaction products. Traces were calibrated using germanium (PDF-00-004-0545) and neodymium hydroxide (PDF-01-070-0214). This step was fundamental in order to select the correct structural files to be used for the following semi-quantitative analysis.

The data files for the Nd-Fe-B hydrides were chosen from literature sources based on their chemical composition [105 [136]. Other phases involved included iron oxides and oxyhydroxides, neodymium hydroxide and hydride. The list of the phases used for the semi-quantification is present in appendix x.

XRPD analysis on the Nd-Fe-B magnets corroded during the Confined-Fluid Flow experiments were performed with the following parameters: 22-85°2θ, 0.01 step size and 4 sec step time. Traces were not smoothed and background not removed before plotting.

XRPD semi-quantitative analysis was performed using Bruker DIFFRAC.TOPAS software; the structural files of the mineral phases previously identified in EVA were downloaded from the CDS-RCS (national Chemical Database Service – Royal Society of Chemistry) online database.
After the first refinements, the phases below 1% were discarded because below the instrument detection limit of 1%. Based on previous quantitative analysis of known mixtures (Quartz+Calcite and Quartz+K-feldspar), the analytical error was calculated to be ±10% relative to the single phase, hence giving an overall accuracy limit of ±1%.

DIFFRAC.TOPAS software calculates automatically the profile fitting errors, but these are regarded as optimistic so the error might be slightly higher. The estimation of the errors for the single phases is optimistic especially considering that these analyses are semi-quantitative and the Nd-Fe-B hydrides have very similar XRPD patterns. In fact, the peak positions of the monohydride results being very close to the non-reacted Nd-Fe-B, as well as the tetrahydride has peak positions closely matching the pentahydride. However, despite the error being quite high on the single NdFeB hydride phases, when the mean HPFUs (Hydrogens Per Unit Formula) are calculated for every single sample, the total error is negligible for the aim of this work.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Semi-Quantitative analysis</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>4.6</td>
<td>±0.3</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>74</td>
<td>±1.6</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{14}$BH$_2$</td>
<td>8.2</td>
<td>±1.3</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{14}$BH$_3$</td>
<td>7.5</td>
<td>±1.2</td>
</tr>
<tr>
<td>Nd$<em>3$Fe$</em>{14}$BH$_5$</td>
<td>3.4</td>
<td>±0.8</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>1.8</td>
<td>±0.3</td>
</tr>
</tbody>
</table>

*Table 3-7: Results of the Semi-quantitative XRPD analysis on the sample Coated Nd-Fe-B from Stack 1 of the Confined-Fluid-Flow experiments. The error calculated by DIFFRAC.TOPAS for the Nd-Fe-B hydrides ranges from ±0.8 to ±1.3.*

3.5.1.4 *SmCo, AlNiCo and Ferrite magnets*

The initial characterisation was made following the same parameters as for the Nd-Fe-B magnets.

Then the analysis was made using the following scan parameters:

- Ferrite: 28-77 2θ range, 0.012 step size and 2 sec step time
- SmCo: 26-75 2θ range, 0.012 step size and 2 sec step time
- AlNiCo: 30-90 2θ range 0.025 step size and 2 sec step time
Since ferrite was not corroded and its peaks were easily recognisable, no internal standard was used and the reflections were calibrated using (PDF-00-054-1176). SmCo also did not require any internal standard as it presents only eight easily recognizable reflections and was calibrated using (PDF-01-081-4607).

AlNiCo alloy presents only three reflections, and so was calibrated using aluminium (PDF-00-004-0787) as internal standard.

### 3.5.2 Magnetic analysis

#### 3.5.2.1 Batch Experiments

In this thesis a materials characterisation-based approach was taken in order to detect and understand the minimal changes happening to the samples.

Magnetic analysis of the Nd-Fe-B, AlNiCo and Ferrite permanent magnet samples extracted from the batch experiments was performed at the Paleomagnetism laboratory at Imperial College London under the supervision of Dr. Adrian Muxworthy and at the Paleomagnetism laboratory at the Grant Institute of GeoSciences at Edinburgh University. SmCo samples were analysed at the Neél Institute (CNRS, Grenoble, France) under the supervision of Prof. Oliver Isnard.

For the hysteresis, remanence and mineral identification using Curie temperature point identification a Princeton Measurements dual-head AGM/VSM (Alternating Gradient Field Magnetometer/ Vibrating Sample Magnetometer) with furnace was used and the high temperature thermomagnetic analyses were carried out in He atmosphere to prevent oxidation upon heating. The magnetic grains were mixed with cement, then attached to the vibrating rod of the instrument and lowered to reach the coils generating the magnetic field. SmCo samples were analysed using a high-field immersion magnetometer (see Section 3.5.2.2).

Hysteresis and backfield curves were fitted using log-Gaussian functions using the best-fit approach and then the parameters ($M_S$, $M_{RS}$, $H_C$, $H_{CR}$) automatically calculated using RockMagAnalizer 1.0 [137]. The analysis of the Curie points was performed using a second derivative approach [137].
From the hysteresis loops, the following parameters were calculated:

- **Mₘᵣ**: Remanence
- **Mₛ**: Saturation remanence
- **Hₖ**: Coercivity

From the backfield curves, the Hcr (Coercivity of remanence, also called remanent coercive force) parameter was calculated.

Magnetites were analysed at the Paleomagnetic Laboratory of the GeoSciences department of Edinburgh University, with the help of Dr. Jenny Tait and Mrs. Myriam Rada Torres, using an Agico Kappabridge susceptibility meter. The magnetite powder was inserted in a glass tube and analysed in a 30-700°C temperature range under argon atmosphere to prevent oxidation. The resulting datasets were analysed with Cureval8 software and plotted using Excel.

### 3.5.2.2 Confined Fluid Flow Experiments

Magnetic analysis on the samples extracted from the Confined Fluid Flow experiments and on the samples from the Sm only and SmCo+bentonite sets of the batch experiments were performed at the Neél Institute (Grenoble, France) under the supervision of Prof. Oliver Isnard.

The materials (raw and reacted) were characterised for Curie Points and magnetization analysis. For the thermomagnetic measurements, a home-made Faraday type balance was used; the magnetic field used was less than 0.1 T. The thermomagnetic measurements were performed with a heating rate of 10 °C/min on powder samples. A sample of 50–100 mg was sealed under vacuum in a small silica tube in order to prevent oxidation of the sample during heating. Nd-Fe-B samples were analysed up to 900°C, SmCo and AlNiCo to 1000°C.

The magnetization measurements of the SmCo type magnets have been performed in magnetic field up to 10 T using the extraction method in an home made experimental set up that has been described elsewhere [138]. Similar equipment running operating in the temperature range from 200 to 850K and magnetic fields up to 7 T was used for Nd-Fe-B and AlNiCo permanent magnets. The saturation magnetization Mₛ was determined through extrapolation from the M vs. 1/H plot.
3.5.3 **ICP-OES analysis**
ICP-OES analysis were performed at the Chemistry department of the University of Edinburgh under the supervision of Dr. Lorna Eades using a Perkin Elmer Optima 5300 DV ICP-OES.

All the samples were scanned to detect major elements (Na, Ca, K, Si, Al) and metal and non-metal cations possibly present in solution (Fe, Co, Cu, Nd, Pr, Ti, Zr, Sm, B and Sr).

3.5.4 **Mössbauer analysis**
Mössbauer analysis were performed at the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI), University of Bayreuth, by Dr. Catherine McCammon.

Preparation of the samples for the analysis was the main challenge regarding this aspect of sample analysis.

The initial idea was to embed the reacted magnetite crystals within epoxy resin inside plastic tubes and then grind them down to the preferred thickness attached to a slide.

The samples needed to be mounted on a thin slide in order to be analysed but glass could not be used because its $\gamma$-ray attenuation coefficient is too high and would have impeded data collection. The first attempt was made using a glass slide and attaching the sample onto it using Crystalbond™ and then removing the sample from the slide in an acetone bath. However, the sample removal caused the sample to bend and could have caused a significant degradation of the resin if the bath lasted for too long. Furthermore, during the grinding process, 50% of the samples could not withstand the shear forces generated by the grinding (Crystalbond™ is known for the weak resistance to shear stress) so became detached.

The subsequent samples were mounted and ground down on a 0.5mm thick PETG (Polyethylene terephthalate glycol-modified) slide; this allowed attachment of the sample to the slide using epoxy resin. The thicknesses of the samples were 100 +/- 20 $\mu$m for the magnetite/maghemite samples and 400 +/- 50 $\mu$m for the bentonite/magnetite samples, assuming 10-50% void fraction in the samples.
4 Results of Batch Experiments

4.1 Introduction
In this chapter the data collected from the samples extracted from the first set of experiments, called batch experiments, are shown.

In these experiments, magnetic materials have been corroded under “extreme” conditions (embedded in bentonite or in solution only), to understand if they react and so have the capability of monitoring a system under “less extreme conditions”.

Testing the reactivity of the materials and their possible usage with an effective but low-cost design was the key focus of the batch experiments. These results are of great help for designing more complex experiments in the near and far future and also for the upscaling of the project; these results were also useful to help understanding the most suitable techniques to be used for the analysis of the samples.

In the batch experiments the magnetic materials (Nd-Fe-B, SmCo, AlNiCo, Ferrite and magnetite) were tested in two different sets (with and without bentonite) and with three different types of solutions (deionized water, high-pH solutions and saline solutions) in a regime of free swelling with no confinement, free pH drift and no recharge of reactants.

For the outline of the experiment refer to section 3.2, whereas for the details about the analysis to section 3.5. In the appendices (chapter 4 folder), the full XRPD traces of magnets and clays are presented. In addition, in this folder also all the thermomagnetic curves of the Nd-Fe-B magnets are shown.

These experiments allowed dividing the analysed material in three categories:

1. Highly reactive magnets (Nd-Fe-B and SmCo)
2. Weakly reactive magnet (AlNiCo)
3. Non-reactive magnets (Ferrite and magnetite)
4.2 Batch Experiments – Nd-Fe-B Permanent magnets
At the time of the extraction, the samples of the NdFeB+bentonite and NdFeB-only (magnets in solution) sets featured clear differences in terms of corrosion of the magnetic phase, precipitation of corrosion-related phases and colour of the matrix.

Figure 4.1: Picture of samples belonging to the NdFeB+bentonite set taken one month after the beginning of the experiment. From left to right samples reacted with deionized water, NaOH, KOH and Ca(OH)\textsubscript{2} solutions. In the first sample, the magnet has been pushed upwards (a) by the swelling bentonite matrix and there is presence of precipitated (b) orange-coloured material (Feroxyhyte/Ferrihydrite?).

Figure 4.2: Picture of samples belonging to the NdFeB+bentonite set taken one month after the beginning of the experiment. From left to right samples reacted with KCl, NaCl, and CaCl\textsubscript{2} solutions. All three feature heavily oxidized magnetic particles, precipitation of orange-coloured (b) material (Feroxyhyte/Ferrihydrite?) and partially swollen matrix (c). The water column, in all three samples, has a yellowish colour due to material in suspension or metals in solution (d).
The signs of corrosion were visible just after one month since the beginning of the experiment (Figures 4-1 and 4-2), with precipitation of orange-coloured material at the solution/matrix interface and formation of haloes surrounding the magnets embedded in matrix.

![Image of samples](image.png)

*Figure 4-3: Picture of samples belonging to the NdFeB+bentonite set taken two months after the beginning of the experiment. From left to right samples reacted with KCl, NaCl, and CaCl₂ solutions. Precipitation of black material (e) (goethite/lepidocrocite?) is present at the solution/bentonite interface and the haloes around the buried magnets are more visible than in Figure 4-2.*

The samples reacted with saline solutions show a clear evolution through time, with an increasing amount of precipitated material at the solution/matrix interface and the production of gas, highlighted by the swollen butyl septa (Figures 4-3 and 4-4). This evolution is related to the partial swelling of the matrix, which left interstitial fluid that allowed the reaction to proceed. The main difference between the three sets of solutions (deionized water, alkaline solutions and saline solutions) was the appearance of the Nd-Fe-B fragments. In the samples treated with alkaline solutions the fragments were still intact, showing oxidation effects, whereas in the samples treated with the other two sets of solutions the magnets were completely disaggregated and the particles surrounded by fine-grained black material.

At the time of extraction, the clay matrix did not show changes in colour for the samples reacted with alkaline solutions and deionized water, but in the samples reacted
with saline solutions a halo of variable thickness was visible around the corroded magnets with a colour degrading from a dark olive green at the interface towards a light yellow/grey (Figure 4-3 and Figure 4-4).

Figure 4-4: Picture of samples belonging to the NdFeB+bentonite set taken after the end of the experiment. From left to right samples reacted with NaCl, KCl, and CaCl$_2$ solutions. NaCl-solution treated sample features tensile fractures partially filled with solution and black coloured material. KCl- and CaCl$_2$-solution treated samples feature partially swollen matrix (c) and presence of black-coloured material precipitated at the solution/bentonite interface. The butyl septa appear all deformed and swollen for presence of hydrogen gas formed by the corrosion of the magnets.

Post-extraction XRPD analysis show a clear change in the crystallography of the magnetic phase, with a shift towards lower diffraction angles of all the peaks of the $\varphi$-phase (Figure 4-5, Figure 4-8, and Figure 4-10) and disappearance of the peaks related to the $\rho$-phase (See Chapter 2.2 for information on the phases of Nd-Fe-B alloys). The $\eta$-phase peak is still present in all samples, although its peak also shifts as well towards lower diffraction angles. The range 35-40°2θ was chosen in order to examine the variations occurring to three of the peaks of the $\varphi$-phase (labelled after Sagawa et al. [81]) and the peak of the $\eta$-phase. The full XRPD traces are displayed in Appendix 4.1.1. Figure 4-5 shows the XRPD traces of the samples treated with alkaline solutions and the samples reacted in Na- and K-rich alkaline solutions only did not show shifts of the diffraction peaks.
Figure 4-5: XRPD traces of the Nd-Fe-B permanent magnets reacted with alkaline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. From bottom to the top raw material (black line), reacted with 0.1M NaOH solution (green line), reacted with 0.1M KOH solution (red line) and Ca(OH)₂ solution (blue line). Thick red (ϕ-phase) and violet (η-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples.

Figure 4-6: Hysteresis loops Nd-Fe-B permanent magnets reacted with alkaline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. The samples reacted within bentonite matrix (b) feature a transition from Pseudo Single Domain-like behaviour (red loop) to superparamagnetic material (green and blue loops). Loop of the raw material in Figure 5-4A.
Figure 4-7: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with alkaline solutions in aqueous media (left column) and within bentonite matrix (right column). These pie charts consider the main magnetic phases only. Passivated samples in NaOH and KOH solutions (left column) feature respectively 98 and 100 wt. % of raw Nd-Fe-B magnet, whereas the other samples a complex composition. The samples reacted within bentonite matrix show a clear predominance of NdFeBH$_2$. The samples reacted with Ca-rich solutions all have a complex composition, with more hydrides present and in higher concentrations of each of the others.
Passivation did not happen for the sample reacted in Ca-rich solution only and in all samples reacted within bentonite matrix. They all display shift of the φ- and η-phase towards lower diffraction angles, with the sample reacted with Ca(OH)$_2$ solution featuring a slightly larger shift. These shifts of the Nd-Fe-B reflections have a clear relationship with the magnetic transitions observed in the same samples (Figure 4-6).

The passivated samples (reacted in NaOH and KOH solutions) feature a transition from single-domain ferromagnetic behaviour to Pseudo Single Domain-like ferromagnetic behaviour (Figure 4-6).

The further corrosion of the alloy is marked by the hydrogenation (Figure 4-7) of the magnet (visible from the shift of the peaks towards lower diffraction angle) is reflected in the sharp transition from the pseudo-single-domain ferromagnetic hysteresis loop to the superparamagnetic hysteresis loop (Figure 4-6) in both the NdFeB-only or NdFeB+bentonite sets.

In general, all samples that exhibited corrosion effects showed complete loss of hysteretic properties, with a transition towards a superparamagnetic behaviour.

**Figure 4-8:** (a) XRPD traces of the Nd-Fe-B permanent magnets reacted with deionized water in solution only. From bottom to the top raw Nd-Fe-B material (black line), then Nd-Fe-B reacted in water only (blue line) and Nd-Fe-B reacted within bentonite matrix (red line). Thick red (φ-phase) and violet (η-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples. (b) Hysteresis loops Nd-Fe-B permanent magnets reacted with alkaline solutions. Loop of the raw material in Figure 5-4A.
The samples reacted with deionized water (Figure 4-8a and Figure 4-9) show greater corrosion effects than the samples reacted with alkaline solution. This is indicated by the greater shifts of the reflections of either the $\phi$- or $\eta$-phase towards lower diffraction angles. As previously seen in Figure 4-6, the increasing corrosion of the alloy is reflected in the hysteresis loops, which have the typical shape of a superparamagnetic material (Figure 4-8–b).

Figure 4-9: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with deionized water in aqueous media (left) and within bentonite matrix (right). This pie chart considers the main magnetic phases only. The sample reacted in bentonite matrix shows a relatively more homogeneous hydrogenation of the alloy, whereas the sample reacted in aqueous media a rather non-uniform hydrogenation with higher percentages of different hydrides.

Figure 4-10: XRPD traces of the Nd-Fe-B permanent magnets reacted with saline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. From bottom to the top raw material (black line), reacted with 1M NaCl solution (green line), reacted with 1M KCl solution (red line) and CaCl$_2$ solution (blue line). Thick red ($\phi$-phase) and violet ($\eta$-phase) lines represent the peak positions in the raw material, whereas the thin, dashed lines represent the peak positions in the corroded samples.
The samples reacted with saline solutions all feature high levels of hydrogenation, which cause a shift (between 0.3 and 0.5°2θ) of the Bragg peaks towards low diffraction angles (Figure 4-10). Again, as seen in Figure 4-5, the highest levels of hydrogenation are seen for the samples reacted in Ca-rich solution, and the samples embedded in bentonite display bigger shifts of the diffraction peaks.

The differences in the scale of peak shifting seen in Figure 4-10 are reflected in the shape of the loops (Figure 4-11-a), with the samples reacted in aqueous media only showing a clean transition from a Pseudo Single Domain-like material (green and red loops) to a superparamagnetic material. The values of saturation magnetization are comparable to the equivalent samples reacted with alkaline solutions (Figure 4-6).

In contrast, the magnets reacted within the bentonite matrix show similar shifts of the Bragg reflections and hence similar hysteresis loops, peculiar of a superparamagnetic material (Figure 4-11-b). Their saturation magnetization values are considerably lower than the equivalent samples reacted with alkaline solutions (Figure 4-6).

Figure 4-11: Hysteresis loops Nd-Fe-B permanent magnets reacted with saline solutions. NdFeB-only set on the left, NdFeB+bentonite set on the right. The samples reacted in solution only (a) show a very nice transition from Pseudo Single Domain-like loop (red and green loops) to a loop typical of a superparamagnetic material (blue), whereas the samples reacted within bentonite matrix (b) all feature loops of superparamagnetic materials. Loop of the raw material in Figure 5-4a.
Figure 4-12: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the magnets reacted with saline solutions in aqueous media (left column) and within bentonite matrix (right column). This pie chart considers the main magnetic phases only. All samples feature complicated compositions with most of the hydrogenated phases present in considerable amounts. Samples reacted in aqueous media on average have higher percentage of raw Nd-Fe-B phase and lower averaged hydrogen content.
From Figure 4-12 it can be seen that the composition of the magnetic grains corroded in saline solutions is more complicated than their counterparts reacted in alkaline solutions, with a higher percentage of NdFeBH$_3$, NdFeBH$_4$, and NdFeBH$_5$ in the samples reacted within bentonite matrix. An unusual feature is the relatively high percentage of unreacted Nd-Fe-B phase in the samples reacted in saline solutions only (Figure 4-12), which display Pseudo Single Domain-like behaviour with higher saturation magnetization (red and green lines) or superparamagnetic with lower saturation magnetization (blue line) hysteresis loops. In contrast, the samples reacted within bentonite matrix all have superparamagnetic hysteresis loops with lower saturation magnetization values.

These results collectively indicate that the magnetic transition from magnetocrystalline-single-domain to Pseudo Single Domain-like material correlates with predominant presence of hydrogenated Nd-Fe-B hydrides with 1-2 hydrogens per unit formula. In contrast, the transition from pseudo-single domain to superparamagnetic material coincides with the predominant presence of hydrogenated Nd-Fe-B hydrides with 3 to 5 hydrogens per unit formula.

The mean absorbed hydrogen per unit formula (HPFU) extrapolated from the results of the XRPD semi-quantification is strongly dependent on the Curie temperatures of the corroded alloys (Figure 4-13). The two experimental datasets appear to be clustered in two very well defined areas, with the only exception of the sample reacted in deionized water only.

I am unaware of any published reference about the behaviour of the magnets upon corrosion. The following paragraphs and the discussion chapter compare the results I collected with other research works that have used other analytical techniques or have analysed materials treated in different ways.

Figure 4-14 shows the relation between average HPFU and coercivity, which demonstrates a trend from the passivated samples towards the most corroded (samples reacted with deionized water and saline solutions), and the differences between samples reacted within bentonite matrix and solution only.
Figure 4-13: HPFU vs. Curie temperature plot. The samples of the NdFeB-only (Nd-only) and NdFeB+bentonite (NdB) set are plotted with pure Nd-Fe-B hydrides [105]. The relative scatter of the samples from this study reflects their impure chemical compositions which causes shifts in temperature. Curie temperature error ±5°C, HPFU estimation error ±0.5.

Figure 4-14: HPFU vs. Coercivity plot. HPFU estimation error ±0.5.
The values of coercivity mostly lie between 5 and 20 Oersted. This may be related to the fact that both pseudo-single-domain and superparamagnetic materials have generally low coercivity values due to the different orientations of the magnetic domains; this makes it easier for an applied external magnetic field to demagnetize the alloy.

The relationship between Curie temperature (Figure 4-13) and coercivity (Figure 4-14) and HPFU suggest a possible dependence of the magnetic properties on the ratio of hydrogenation and/or presence of bentonite matrix. However, as the magnets did not corrode under controlled conditions (controlled hydrogen pressure or N-purged atmosphere) is not possible to confirm that this dependence is real.

Following the studies by Day et al. [128] and Dunlop [129] mentioned in Chapter 2.6, a similar graphical approach was taken to understand the grain size (or composition) dependence of the magnetic properties of the corroded Nd-Fe-B magnets.

The plot in Figure 4-15 shows no effect of the presence/absence of bentonite matrix on the Mrs/Ms and Bcr/Bc ratios, but suggests a possible division in the Pseuso Single Domain-Multi Domain areas between the samples corroded in deionized water and Ca- and Na-rich alkaline solutions (high Hcr) and those samples corroded in saline solutions or K-rich solutions (low Hcr).

The Day/Dunlop plot (Figure 4-15) [128] shows a clear trend from the less corroded magnet sample, sitting in the Single Domain area, to the most corroded samples, sitting in the Multi-Domain area or along the Pseudo Single Domain/Multi Domain boundary for the Mrs/Ms; two samples are positioned in the Pseudo Single Domain area.

Day et al. [128] and Dunlop [129] suggest that the samples (or mixtures) falling in the Multi Domain or Pseudo Single Domain field have larger grain size or predominance of “soft” magnetic phase in the mixture. However, an increasing size of the domains of the φ-phase from 3 to 30 μm is unlikely even in a completely hydrogenated sample where only Nd$_2$Fe$_{14}$BH$_5$ phase is dominant.

This paradox may be resolved considering that in literature a drastic decrease of coercivity is reported for sintered magnets with grain size smaller than 3μm [92]; hence, the decrease of coercivity may be related to the formation of extremely small
(<1μm) ferromagnetic grains of hydrogenated Nd-Fe-B alloy around a core of unreacted material.

Figure 4-15: Mrs/Ms vs. Hcr/Hc plot after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129]. The sample circled in blue is, considering the previous plots and figures (Figure 4-6 and Figure 4-14), a problematic point. From X-ray diffraction and Curie temperature data, the sample did not suffer high levels of corrosion and so should not fall in that area. The sample, during hysteresis analysis, was not saturated and hence its parameters are not correct. The boundaries between Single Domain, Pseudo Single Domain and Multi Domain areas are in dashed lines because they represent the limits given for mixtures of synthetic mixtures of magnetites and titanomagnetites with known grain sizes. The samples in this experiment do not have a known grain size and have very heterogeneous chemical and physical properties. The red box discriminates the cluster of samples reacted in deionized water and alkaline solutions, whereas the green box the samples reacted with saline or K-rich solutions.

In addition to the grain size of the ϕ-phase, other two parameters must be taken into account in the analysis of these samples: their chemical heterogeneity and the presence of other ferromagnetic (magnetite, maghemite or defected spinels) or paramagnetic phases among the corrosion-related products.

In the thermomagnetic analysis, a number of Curie points (Figure 4-16) reflecting the presence of Fe-rich corrosion products precipitates, like magnetite, goethite or defected iron spinel [139]. Hence, the XRPD semi-quantification on the corroded magnets also considered these accessory phases, although their peaks were not visible
in the XRPD traces, as their crystallite sizes would be too small, or in too small concentrations, to produce distinct peaks. Fe oxyhydroxides such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), feroxyhyte (δ-FeOOH) and ferrihydrite (Fe$_{3+}$O$_7$•0.5(H$_2$O)) are cryptocrystalline or amorphous so they contributed to the amorphous slope or the background hump of the traces. Given that precise identification of the Fe-(oxy)hydroxide phases is particularly difficult in low temperature systems with free-pH drift, in this analysis the sum of the Fe oxyhydroxides, Fe oxides and Nd-rich phases is presented rather than the abundances of single species. Other thermomagnetic curves are presented in Appendix 4.1.2.

Figure 4.16: Three examples of results of thermomagnetic analysis. Red curves represent the heating stage and the blue curves the cooling stage. (a) passivated Nd3-only; Curie temperature 311°C (b) corroded NdB7 sample; Curie temperature 376°C (c) corroded NdB3 sample; Curie temperature 376°C. The green circles highlight the areas of the heating curves generated by the presence of Fe oxyhydroxides or defected Fe oxides. All samples present a Curie point between 236-246°C. In the literature, Curie points in this area have been related to presence of defected iron oxides or defected iron oxides solid solutions. With the exception of the passivated sample, all other curves present an irreversible behaviour after heating, testifying the metastability of the Nd-Fe-B hydrides. The asterisks mark the presence of a rise to high susceptibility values called Hopkinson peak.
All thermomagnetic curves present a Curie point in an area comprised between 236-257°C (Figure 4-16). These points have been related to presence of defected iron oxides or defected iron oxides solid solutions, which are stable at room temperature but are transformed in more stable oxides upon heating, causing the heating curve to increase its magnetization towards high temperature instead of decreasing it. This increase in magnetization can also be caused by the transformation of Fe-oxyhydroxides into more stable oxides upon heating or decomposition of Nd-Fe-B hydrides into REE oxides and Fe-rich phases. Hence, the Curie point measured at the highest temperatures represents also the transformed metastable oxides/oxyhydroxides or decomposed Nd-Fe-B hydrides. The presence of defined low Hopkinson peaks (Figure 4-16 c) and higher Hopkinson peaks (Figure 4-16 b) is related to Multi Domain or Superparamagnetic grains of the phases related to the Curie temperature ahead.

The abundance of Fe oxyhydroxides (Figure 4-17) is directly related to the solution composition, and increases greatly in the saline environments, consistent with a more extensive corrosion of the magnets linked to a higher chloride activity.

\[\text{Figure 4-17: Abundance of Nd-Fe-B corrosion products in terms of total Fe oxides (magnetite, maghemite, hematite and iron α), total Fe oxyhydroxides (goethite, lepidocrocite, ferroxyhyte and ferrihydrite) and Nd-rich phases (Nd(OH)\textsubscript{3}, NdOH and NdH\textsubscript{2}) in NdFeB-only (a) and NdFeB+bentonite (b) sets. The dashed lines represent the trend line of the respective mineral groups. The y axis in in wt. %. Abundances were calculated from XRPD semi-quantitative data. Errors estimated ±1%.}\]
The abundances of Nd-rich phases and Fe oxides is generally constant in all samples of the Nd only set with exception of the sample reacted in CaCl₂ solution (Figure 4-17, a). Passivated and less reacted samples show generally lower percentages of accessory corrosion-related phases. The magnets corroded within the bentonite matrix show a remarkable increase of percentages from the samples reacted with alkaline solutions compared with those reacted with saline solutions (Figure 4-17, b) and deionized water.

The presence of the bentonite matrix clearly influences the corrosion of the Nd-Fe-B magnets, causing an on-average higher hydrogenation than in the control samples, which contributes to the transition from magnetocrystalline-single-domain magnetic properties to superparamagnetic properties. This transition causes a sudden decrease of coercivity and increase of the Curie temperature of the alloy.

The samples reacted with saline solutions within bentonite matrix show higher corrosion effects in the K- and Ca-rich solutions, consistent with higher corrosivity of K- and Ca-exchanged bentonites [80].

4.2.1 Summary and Discussion
From the hysteresis plots in figure 4-6, 4-8 and 4-11, and the Day/Dunlop plot is clear that the progressive corrosion of the alloy leads to the transition from a single-domain to Pseudo Single Domain-like and to a superparamagnetic magnetic behaviour. In general, all the samples that had not been passivated show a great decrease in remanence and coercivity.

In previous researches [92] was observed how the coercivity of the Nd-Fe-B powders decreases with average grain size <3μm. Hence, the magnetic properties of the corroded samples here studied might have been affected by an average reduction of the grain size of the main magnetic phase.

The comparison of hysteresis with XRPD data demonstrated how the transition from one domain another is related to the predominance of Nd-Fe-B hydrides with less (1-2) or more (3-5) hydrogens per unit formula.

These observations lead to the question of how the corrosion takes place and why it leads to the transition towards a superparamagnetic Nd-Fe-B hydride.
A likely explanation is provided below with reference to figure 4-18, 4-19 and 4-20.

The initial Nd-Fe-B alloy is composed (Figure 4-18) by grains of ferromagnetic Nd$_3$Fe$_{14}$B phase ($\phi$-phase), with aligned magnetic domains, randomly dispersed grains of Nd$_{1+x}$Fe$_4$B$_4$ phase ($\eta$-phase) and interstitial Nd$_2$Fe$_7$B$_6$ phase ($\rho$-phase).

The first step of the corrosion is the development of a galvanic couple between the $\rho$-phase and the $\phi$-phase (or $\eta$-phase) [98], with the first considered the anode and the second the cathode. The anode is corroded first due to its high galvanic activity (and lower electrode potential). Hence, a metal (or two coupled alloys as in this case) generates an electric field due to the difference in electrode potential between the anode and the cathode. Considering an Nd-Fe-B alloy in contact with a 1M NaCl solution, the Cl$^-$ ions are adsorbed at the metal/solution interface and their charge balanced towards the solution by counterions of the opposite charge (Na$^+$), forming an Electrical Double Layer (EDL), which increases the potential difference of the system and hence the corrosion of the alloy.

Figure 4-18: Schematic illustration of a raw Nd-Fe-B alloy before corrosion (left) and as corrosion starts (right). The initial alloy is composed by ferromagnetic grains ($\phi$-phase) with magnetic moment vectors all aligned in one direction. These grains and surrounded by a paramagnetic interstitial phase ($\rho$-phase) that corrodes first causing the ferromagnetic grains to exfoliate. The exfoliation process leads the magnetic moment vectors to not be aligned anymore, causing the transition from a magnetocrystalline-single domain phase to a pseudo-single-domain phase. Blue arrows indicate the directions of the magnetic moment vectors.
Figure 4-19: Schematic representation of the corrosion process on an \( \text{Nd}_2\text{Fe}_{14}B \) (q-phase) grain. The interstitial phase (p-phase) is corroded in accordance with Equation 4-1, and the corrosion-related phases precipitate at the grain boundary. The hydrogen produced at anode site is partially absorbed by the q-phase to form layered Nd-Fe-B hydride complexes and partially diffuses as hydrogen gas.

The p-phase may be corroded, for example, following this chemical equation:

Equation 4-1: \( \text{Nd}_2\text{Fe}_7\text{B}_6(s) + 18\text{H}_2\text{O} + 8\text{O}_2 \rightarrow 2\text{Nd(OH)}_3(s) + \text{Fe}_3\text{O}_4(s) + 4\text{FeOOH}(s) + 6\text{B(OH)}_3(aq) + 6\text{H}^+(aq) + \text{H}_2(g) \)

The corrosion of the p-phase causes the reduction of water, with production of hydroxyl groups and hydrogen. Part of this hydrogen is absorbed by the main magnetic phase (q-phase) to create layers of different hydrides around a core of unreacted \( \text{Nd}_2\text{Fe}_{14}B \) (Figure 4-19). The extent of the p-phase corrosion determines the amount of hydrogen produced and hence the type of hydride produced (Figure 4-19). With the corrosion of the interstitial phase the exfoliation of the main magnetic phase proceeds...
(Figure 4-18) until the magnets are completely disaggregated but, at the same time, hydrogenation of the φ-phase occurs; this causes a progressive misalignment of the magnetic moment vectors, registered by the hysteresis loops through the transition from magnetocrystalline-single domain to pseudo-single-domain loops. When the magnets are completely disaggregated or have reached high levels of hydrogenation, the transition to a superparamagnetic material is reached. The layers of hydrides are made of microcrystals (each one is a ferromagnet) of Nd-Fe-B hydride, each with its own magnetic moment vector (Figure 4-20). They are not aligned, and so the magnet grain loses its main characteristics, which are a very high uniaxial magnetocrystalline field, and high coercivity and remanence.

![Figure 4-20: Schematic representation of the formation of micro-crystals within the hydride layers around the core of unreacted Nd-Fe-B. Each micro-crystal has its own magnetic moment vector, not aligned with the magnetic vector of the raw Nd-Fe-B core.](image)

The transition from Single Domain to Pseudo Single Domain-like/Superparamagnetic behaviour cannot be related to the exfoliation, because this process alone does not change the grain size of the ferromagnetic grains or the formation of smaller domains. Instead, hydrogenation of the main magnetic phase can be interpreted to be the main driving force for the Single Domain/Pseudo Single Domain-like and Pseudo Single Domain-like/Superparamagnetic transitions because it promotes the formation of rims of hydrides with smaller domain sizes. In this thesis the transitional area between Single Domain and Multi Domain/Superparamagnetic is called Pseudo Single Domain-like because the material resembles the hysteretic behaviour of a Pseudo
Single Domain mixture or grain but is not related to a volumetric expansion of the grain, which is otherwise demonstrated by Day *et al.* [128] and Dunlop [129].

Day *et al.* [128] related the decreasing coercivity to a big grain size of the magnetites or to higher proportions of “soft magnetic phase” in mixtures. The term Soft magnetic material is related to a material that is easily magnetizable (or demagnetizable) and has a low coercive field.

The change in the hysteretic behavior of corroded Nd-Fe-B from truly Single-Domain (typical of a “Hard” ferromagnet as the unreacted Nd-Fe-B) to Multi-Domain may be also related to an increasing percentage of corrosion-related superparamagnetic particles. These possess a behavior, under an applied magnetic field, that resembles that of an increasing percentage of “Soft” ferromagnets as described by Day *et al.* [128] and Dunlop [129]. The variable values of saturation magnetization calculated for the samples is mainly due to different proportions on non-ferromagnetic materials formed upon corrosion. The presence of grains of smaller size is confirmed by the calculation of the Single Domain to Superparamagnetic transition using the blocking volume equation in according with the formula from Dunlop and Özdemir [140]. Giving a relaxation time ($t_m$) of 1s and remanence ($M_r$) 145 Am$^2$/kg, the calculated Single Domain/Superparamagnetic transition falls at ca. 3 nm.

Bentonite may play a considerable role as corrosion-enhancer principally because, during the swelling process, a Diffuse Double Layer (DDL) is formed, and this increases the localized potential in the sample. In other words, the DDL generated at the bentonite surface couples with the opposite polarity EDL at the magnet’s surface, creating a micro-battery cell, which leads to increased aggressivity of the solution.

This section has demonstrated how Nd-Fe-B permanent magnet reacts quickly with the permeating fluids and how the changes to its magnetic properties appear to be related to the composition of those solutions. Based on the results given, and even given the intrinsic complexity of the system and the technical difficulties to resolve it, we can consider Nd-Fe-B permanent magnets as suitable candidates for monitoring the EBS and detecting water saturation of the bentonite buffer.
They appear to have good potential for detecting intrusion of saline or alkaline solutions in the EBS, an important object for further study in the future.

4.3 Batch Experiments - SmCo permanent magnets

At the time of the extraction, all samples from SmCo+bentonite and SmCo-only (magnets in solution) sets showed signs of corrosion, with traces of precipitation of orange-coloured material in the samples reacted with saline solutions (Figure 4-21). The samples reacted with alkaline solutions or deionised water showed dark grey-coloured surfaces and precipitation of fine black materials around the magnets.

![Figure 4-21: From left to right samples of the SmCo+bentonite set reacted with 1M NaCl, 1M KCl and 1M CaCl₂ solutions. Only the first sample features complete swelling of the matrix whereas the other two only a 200% swelling as observed in all the other experimental sets. One of the main characteristics is the presence of abundant quantities of red/orange precipitates at the solution/air interface and at the solution bentonite interface.](image)

XRPD analysis on the corroded magnets show how the corrosion process initially attacked the interstitial phase (Sm₂O₃), the peak of which (29.7°2θ) is not present in all run samples (Figure 4-22 and Figure 4-23). The interstitial phase acts as an anode, similarly to the ρ-phase in the Nd-Fe-B magnets, and is corroded first.

The samples of the SmCo-only set (Figure 4-22) show negligible signs of corrosion of the main magnetic phase, with the only exception being the 300 reflection of the sample reacted in KCl solution. On the other hand, the samples reacted within bentonite matrix (Figure 4-23) show decreases in the intensities of the 300, 220 and
223 reflections, which are more accentuated in the samples reacted with saline solutions.

Figure 4-22: XRPD traces of SmCo permanent magnets reacted in aqueous solutions only (Sm only set). Intensity of the peaks reduced by two times for ease of display. y axis in counts/sec.

Figure 4-23: XRPD traces of SmCo permanent magnets reacted in bentonite matrix (SmCo+bentonite set). Intensity of the peaks reduced by two times for ease of display. y axis in counts/sec.
In terms of magnetic signatures, comparison between the samples reacted with deionised water and the starting SmCo permanent magnet (Figure 4-24) show that the reacted samples exhibit a coercive field one order of magnitude lower than the starting SmCo magnet (2.85T). The coercive field is at 0.36T for the sample reacted in solution only (Figure 4-24A) and 0.83T for the sample reacted within bentonite matrix (Figure 4-24B). The remanence is lower for the SmB1 sample 50.1 (Am²/kg) than the Sm1 only sample (61.7 Am²/kg).

The decrease in the hard magnetic phase is greater in the Sm1-only sample than that in the SmB1 sample. In both cases, the decrease is not compensated by increase in soft magnetic phases. The higher remanence in the Sm1-only sample is explained by a slightly greater amount of soft magnetic phase product. It is interesting to note that either remanence or saturation magnetization have been reduced by more than 1/3 from the raw material (99 Am²/kg), indicating the formation of non-ferromagnetic materials (paramagnetic, canted-antiferromagnetic or antiferromagnetic materials).

Magnetic analysis on the samples corroded with alkaline solutions (Figure 4-25 A and B) show that these have behaviour similar to the reacted samples in Figure 4-24.
The samples of the SmCo-only set (Figure 4-25A) feature similar coercive field values between 0.88T (Sm4-only) and 0.36T (Sm3-only); they exhibit a decrease in coercive field of one order of magnitude. They also feature similar remanence (82.7, 84.4 and 78.8 Am²/kg respectively) and saturation magnetization values (100, 97.2 and 103 Am²/kg respectively).

![Figure 4-25: Hysteresis loops of the samples of the Sm only (A) and SmCo+bentonite set (B) reacted with alkaline solutions. The black loop refers to the raw SmCo26 permanent magnet, the green loops the samples reacted with 0.1M NaOH solution, the red loop the sample reacted with 0.1M KOH solutions and the blue loops the samples reacted with 0.05M Ca(OH)₂ solutions.]

The samples of the SmCo+bentonite set (Figure 4-25B) exhibit a wider range of coercivity values, from 0.23 T for SmB3 to 0.6T for SmB4 to 1.31T for SmB5. Remanence values fall from 99 Am²/kg in the raw sample to 65 Am²/kg in SmB5 and 50.1 and 54 Am²/kg for SmB4 and SmB3 respectively. Saturation magnetization follows the same trend going from 103 Am²/kg in the raw sample to 82.3 Am²/kg in SmB5 and to 69.8 and 66 Am²/kg for SmB4 and SmB3 respectively.

The samples reacted in saline solutions (Figure 4-26A) feature similar hysteresis loops to the samples in Figure 4-24 and Figure 4-25. Again, the samples from the SmCo-only set exhibit one order of magnitude smaller coercive fields than the starting material (0.48 T for Sm2-only, 0.36T for Sm7-only and 0.59T for Sm8-only). Values of remanence are more scattered, from 51.66 for SmCo-only to 62.9 for Sm8-only and 70.89 Am²/kg for Sm2-only. Saturation magnetization is between 84 and 99 Am²/kg.
Figure 4-26: Hysteresis loops of the samples of the Sm only (A) and SmCo+bentonite set (B) reacted with saline solutions. The black loop refers to the raw SmCo26 permanent magnet, the green loops the samples reacted with 1M NaCl solution, the red loop the sample reacted with 1M KCl solutions and the blue loops the samples reacted with 1M CaCl$_2$ solutions.

The samples from SmCo+bentonite set reacted in saline solutions (Figure 4-26B) exhibit a different behaviour to their counterparts of SmCo-only set, with higher coercivity values (0.68T for SmB7 and SmB8 and 2.26T for SmB2) and lower remanence values (30.6 Am$^2$/kg for SmB2, 54.2 Am$^2$/kg for SmB7 and 48.2 Am$^2$/kg for SmB8). Saturation magnetization falls to 49 Am$^2$/kg for SmB2, with the highest value of 74 Am$^2$/kg for SmB7.

The hysteresis analysis shows clearly that the SmCo magnets react all under the conditions applied, leading to considerable variations especially of the coercive field and remanence.

The SmCo magnets embedded in bentonite feature generally lower remanence and saturation magnetization than the samples reacted in solution only, indicating that under those specific conditions the formation of non-ferromagnetic phases might be favoured, whereas in the SmCo-only samples the formation of soft magnetic phases is possible. It is notable that the SmCo+bentonite samples feature generally higher coercivity, indicating that the main hard magnetic phase is better preserved. In this case, the precipitation of non-ferromagnetic phases on the magnet surfaces could act to retard the progress of corrosion.
4.4 Batch Experiments - AlNiCo permanent magnets
At the time of their extraction, the samples from AlNiCo+bentonite and AlNiCo-only (magnets in solution only) sets reacted in saline solution showed intense corrosion effects, marked by the precipitation of orange/red coloured materials on the magnet’s surface or at the solution/bentonite interface (Figure 4-28). The samples of the AlNiCo+bentonite set reacted with saline solutions all feature a variation in the colour of the bentonite matrix and precipitation of abundant secondary phases, whereas the samples reacted in deionized water and alkaline solutions only featured weak oxidation of the surface and pale colour haloes around the fragments embedded in the matrix (Figure 4-27).

These magnets did not show disaggregation in particles but instead featured the formation of dark coatings and precipitation of secondary corrosion-related phases. The identification of these phases via XRPD has not been possible, as they were amorphous and/or nanocrystalline. However, based on the chemistry of the magnets and the analysed solutions, these phases are likely to be Cu-, Fe- or Al-chlorides.

![Figure 4-27](image)

*Figure 4-27: From left to right, samples of the AlNiCo+bentonite set reacted with deionized water, 0.1M NaOH, 0.1M KOH and 0.05M Ca(OH)$_2$ solution. The samples feature all complete swelling of the bentonite matrix, with formation of tensile fractures.*

AlNiCo fragments reacted in solution-only feature the same characteristics as the samples reacted within bentonite matrix.
In this section, the XRPD traces are not shown because this alloy has only three reflections in the 2-80°2θ range and they do not provide useful information on the alloy corrosion. The traces can be examined in Appendix (4.3.1) and more information on the alloy structure in Section 2.4.

Figure 4-28: From left to right, samples of the AlNiCo+bentonite set reacted with 1M NaCl, 1M KCl and 1M CaCl₂ solutions. Only the first sample features complete swelling of the matrix whereas the other two only a 200% swelling as observed in all the other experimental sets. One of the main characteristics is the presence of abundant quantities of red/orange precipitates at the solution/air interface and at the solution bentonite interface. The bentonite matrix presents an orange colour at the interface gently fading towards a yellow/pale-olive-green colour towards the untouched matrix.

Hysteresis loops of the AlNiCo fragments reacted in either within bentonite matrix or aqueous solution only all feature a shape typical of a pseudo-single-domain magnetic material (Figures 4-29, 4-30 and 4-31).

The coercivity values are close for all the samples but the remanence values vary in intensity, coherently with the saturation remanence. This is related to the fact that it was not possible to analyse samples with the same sizes and weights. Hence, it is useful to study the behaviour of this alloy using the ratios of the hysteresis parameters Mrs/Ms and Hcr/Hc, considering that these change in accordance with the size of the magnetic domains and not the size of the sample.
Figure 4-29: Hysteresis loops of AlNiCo samples reacted in Na-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.

Figure 4-30: Hysteresis loops of AlNiCo samples reacted in K-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.
Figure 4-31: Hysteresis loops of AlNiCo samples reacted in Ca-rich solutions. Loop of the raw material in Figure 5-10A. AlNiCo-only set on the left, AlNiCo+bentonite set on the right.

Figure 4-32: Mrs/Ms versus Hcr/Hc after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129]
The diagram in Figure 4-32 shows the AlNiCo-only and AlNiCo+bentonite sets samples plotted in Day-Dunlop [128] [129] space. In comparison with the raw alloy (ratios calculated based on the manufacturer’s data), all samples suffered a shift from a single domain to a pseudo-single-domain behaviour. Although the reacted samples plot close together, the samples reacted in saline solutions feature slightly higher shifts than the samples reacted with deionized water and alkaline solutions.

The transition from single-domain to pseudo-single-domain could be related to an increasing domain strain due to the development of corrosion-related deformation. Whilst most of the samples belonging to the two different sets but reacted with the same solutions feature similar Day-Dunlop ratios, the samples reacted with 0.05M Ca(OH)\(_2\) solution plot well away from each other, at the opposite ends of the data cluster and with the sample reacted in bentonite recording the lowest Mrs/Ms and highest Hcr/Hc. This difference could reflect the formation of Ca-exchanged montmorillonite in this AlNico+bentonite sample set.

### 4.5 Batch Experiments - Ferrite permanent magnets
At the time of the extraction, all samples belonging to the Ferrite-only set and Ferrite+bentonite set showed no trace of corrosion on the surface of the magnets. Similarly to the previous experiments bentonite showed volume expansion up to 300% with alkaline solutions and deionized water (Figure 4-33a) and up to 200% with saline solutions (Figure 4-33b).

*Figure 4-33: (a) Sample FeBW5 (0.5M Ca(OH)\(_2\)) solution (b) Sample FeBW8 (1M CaCl\(_2\)) solution.*
The Ferrie+bentonite set showed the same characteristics of the bentonite matrix as those observed in the control samples (i.e. bentonite reacted without magnets) and no colour haloes were visible, even close to the surface of the magnets.

The fragments of ferrite magnets were intact and no exfoliation or pitting corrosion was visible, for both Ferrite-only and Ferrite+bentonite sets.

![XRPD traces of Ferrites reacted in aqueous solutions only (Ferrite-only set). Intensity of the peaks reduced by four times for ease of display. y axis in counts/sec.](image)

**Figure 4-34**: XRPD traces of Ferrites reacted in aqueous solutions only (Ferrite-only set). Intensity of the peaks reduced by four times for ease of display. y axis in counts/sec.

XRPD analysis confirmed the visual appearance of the samples. Bragg peaks of the ferrites did not show any shift along the horizontal axis due to variations of the cell parameters (Figure 4-34 and Figure 4-35). The lower (but constant throughout the trace) intensity of the peaks registered for the sample treated with 0.05M Ca(OH)$_2$ solution (Figure 4-35) is related to the thickness of the sample only.
On these samples only hysteresis and backfield analysis were performed, given that the XRPD traces did not show any presence of additional corrosion-related phases. Figure 4-36 shows the hysteresis loops of ferrite magnets reacted with Na-rich solutions with and without bentonite matrix respectively. The samples reacted with deionized water are taken as a reference baseline for comparison.
Figure 4-36: Hysteresis loops of Ferrite samples reacted in Na-rich solutions. Ferrite-only set on the left, Ferrite+bentonite set on the right.

Figure 4-37: Hysteresis loops of Ferrite samples reacted in K-rich solutions. Ferrite-only set on the left, Ferrite+bentonite set on the right.

Figure 4-37 shows hysteresis loops of ferrite magnets reacted with K-rich solutions without and with matrix respectively. As seen for the hysteresis loops of the samples reacted in Na-rich solutions (Figure 4-36), variations in Mrs and Hc are minimal and
the shapes are very similar, indicating that the nature of the ferromagnetic material has not changed.

All the hysteresis loops (Figures 4-36, 4-37 and 4-38) show square pot-bellied shapes typical of ferromagnetic materials, with no differences in coercivity (Hc) and minimal differences in saturation remanence (Ms) and remanence (Mrs). Hence, the different solutions did not have any appreciable corrosion effect on ferrite magnets based on the evidence from XRPD or magnetic analysis. Noting that the shape of the hysteresis loops is affected by the shape of the analysed grains and not by the intrinsic magnetic properties, and given that the samples did not have uniform shapes and the same weight, it is useful once again to plot the dimensionless ratios Mrs/Ms vs. Hcr/Hc (Figure 4-39).

The Day/Dunlop plot in Figure 4-39 shows how all ferrite samples fall in the Single Domain area, as expected for a synthetic ferromagnet. A broad scatter is visible on the vertical axis between 0.9 and 0.5, but this does not correlate with fluid composition. This scatter may reflect a dependence of Saturation Remanence (Ms) on the grain size.
of the material, on the shape of the specimens or to different amounts of “soft” magnetic phases in the various samples.

![Figure 4-39: Mrs/Ms vs. Hcr/Hc plot after [128] with Single Domain/Pseudo Single Domain and Pseudo Single Domain/Multi Domain limits drawn after [129].](image)

### 4.6 Batch Experiments - Magnetite

At the time of extraction, the samples of the BMα, BMαW6b, BMβW6 sets and the control samples of the Kirmag set exhibited negligible evidence of evident traces of corrosion of the magnetite or Fe-enrichment of the clay matrix.

The reaction kinetics of magnetite under the environmental and chemical conditions of the batch experiments are known to be very slow and the changes between the raw material and the reacted magnetite were expected to be negligible over the duration of these experiments.

The magnetite samples were investigated with XRPD, Mössbauer and magnetic susceptibility techniques in order to detect even small changes in mineral chemistry and relate it to any variations in its magnetic properties.
Mössbauer datasets (Figure 4-40) obtained on the experimented magnetites were fitted by Dr. Catherine McCammon (Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI) - University of Bayreuth) and from the resulting data the ratios of sextet areas \( R = \frac{S(\text{Fe}^{2.5+})}{S(\text{Fe}^{3+})} \) and the oxidation parameter \( x = \frac{(1.8-R)}{(5.4+5R)} \) [141] were calculated. Mössbauer results are affected by a series of errors related to sample thickness and density, and by sample porosity.

In this section the results of the three experimental sets are presented in three different sub-sections, one for the magnetite only control samples (Kirmag set), one for the time-dependent experiments (BMαW6 and BMβW6 Feb-Jun sets) and one for the bentonite/magnetite mixtures reacted for five months (BMα set).

Only the most significant results are displayed in this section. The full datasets can be found in Appendix (4.5.1).

**Figure 4-40:** Fitted Mössbauer spectrum of sample Kirmag W8b (control sample not sieved reacted with 1M CaCl₂ solution).
4.6.1 Kirmag set – Control Samples

The samples from the Kirmag set were reacted in ‘solution-only’ for five months at 70°C. Only the bulk crushed sample (b) was used for this set.

The susceptibility curves (samples reacted in Na-rich solutions and W6 shown in Figure 4-41) feature the typical behaviour for magnetite or weakly oxidised magnetite, with a susceptibility drop between 580°C (pure magnetite) and 600°C (oxidized magnetite) and a fully reversible susceptibility after heating, as is visible from the perfect fitting of the heating and cooling curves.

![Figure 4-41: Susceptibility curves for samples of the Kirmag set reacted in Na-rich solutions. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C.](image)

These samples have oxidation parameter, x, between 0.05 and 0.18 (Table 4.1), consistent with the formation of an initial mixed phase with less Fe²⁺ and more cation vacancies than the original magnetite [121]. The difference registered by the oxidation parameter x is reflected in the Curie temperatures of the magnetites (bold numbers in Table 4.1) and well demonstrated in Figure 4-42.
Figure 4-42: Oxidation parameter ($x$) vs. Curie Temperature ($T_c$) diagram for the samples of Kirmag set. The red line represents the increasing Curie temperature of the magnetites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution chemistry</th>
<th>$T_c$ (°C)</th>
<th>$R$</th>
<th>$x$</th>
<th>Magnetic Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirmag W1</td>
<td>deionised water</td>
<td>585 - 587</td>
<td>0.51</td>
<td>0.16</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W2</td>
<td>1M NaCl</td>
<td>583 - 585</td>
<td>1.15</td>
<td>0.05</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W3</td>
<td>0.1M NaOH</td>
<td>585</td>
<td>0.77</td>
<td>0.11</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W4</td>
<td>0.1M KOH</td>
<td>580 - 584</td>
<td>1.19</td>
<td>0.05</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W5</td>
<td>0.01M Ca(OH)2</td>
<td>587 - 589</td>
<td>0.42</td>
<td>0.18</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W6</td>
<td>mixed solution</td>
<td>585 - 586</td>
<td>1.16</td>
<td>0.05</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W7</td>
<td>1M HCl</td>
<td>550 - 595</td>
<td>0.40</td>
<td>0.18</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>Kirmag W8</td>
<td>1M CaCl2</td>
<td>586 - 590</td>
<td>0.40</td>
<td>0.16</td>
<td>moderately oxidised magnetite</td>
</tr>
</tbody>
</table>

Table 4-1: Curie temperatures, Sextet ratio ($R$) and oxidation parameter ($x$) for the magnetites of the Kirmag set. All the samples result being either weakly or moderately oxidised magnetites. For the composition of the mixed solution refer to W6 in Table 3.2.

4.6.2 BMα Set – Five month-long experiment
The samples from the BMα (bentonite/magnetite non-compressed) set were reacted in pulverised bentonite for five months at 70°C. Three magnetite grain sizes were used in this set to evaluate if grain size affected magnetic response. For the grain size description refer to Chapter 3.2.1.

The susceptibility curves show the classic drop between 580 and 590°C as seen for the control samples of the Kirmag set. In Figure 4-43, it is apparent that those samples containing a fine-grained fraction (a and b) also feature a small drop in magnetic susceptibility between 350 and 355°C. This drop is visible in all the samples containing
fine-grained magnetite reacted with deionised water (Figure 4-43) and saline solutions (Figure 4-44). The samples reacted with alkaline solutions feature the standard susceptibility curve for magnetites (Figure 4-45).

Figure 4-43: Susceptibility curves for samples of the BMα set reacted in deionised water. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.

Figure 4-44: Susceptibility curves for samples of the BMα set reacted in 1M NaCl solution. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.
The susceptibility curves showing the drop at ca. 350°C during the heating stage do not show the same step in the cooling curve. This shows that that the phase responsible for the susceptibility drop is likely irreversibly transformed in a more stable mineral.

Figure 4-45: Susceptibility curves for samples of the BMa set reacted in 0.1M NaOH solution. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. a: <30 μm, b: non-sieved magnetite, c: >120 μm.

Table 4-2: Curie temperatures, Sextet ratio (R) and oxidation parameter (x) for the magnetites of the BMa set reacted with deionised water and alkaline solutions. All the samples result being either weakly or moderately oxidised magnetites.
The irreversibility of the transformation of the phase with a Curie temperature, $T_C$, of 350-355°C is coherent with the possible presence of metastable $\gamma$-Fe$_2$O$_3$ (maghemite) which, on a laboratory timescale, in the dry state and at ambient temperature converts into stable $\alpha$-Fe$_2$O$_3$ (hematite) at a temperature around 350°C [142]. Conversion temperature of maghemite are also reported between 250 and 900°C [143] [144] [145].

The difference registered by the oxidation parameter $x$ is once again reflected in the Curie temperatures of the magnetites (bold numbers in Table 4-2) as seen in Figure 4-46.

**Figure 4-46: Oxidation parameter ($x$) vs. Curie temperature ($T_C$) diagram for samples of BMα set reacted with deionised water and alkaline solutions.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution Chemistry</th>
<th>$T_C$ (°C)</th>
<th>350°C $T_C$ Phases</th>
<th>$R$</th>
<th>$x$</th>
<th>Magnetic Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMαW2a</td>
<td>1M NaCl</td>
<td>586-588</td>
<td>yes</td>
<td>1.71</td>
<td>0.006</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW2b</td>
<td>1M NaCl</td>
<td>588-590</td>
<td>yes</td>
<td>1.24</td>
<td>0.04</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW2c</td>
<td>1M NaCl</td>
<td>NA</td>
<td>no</td>
<td></td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td>BMαW7a</td>
<td>1M KCl</td>
<td>588-589</td>
<td>yes</td>
<td>0.99</td>
<td>0.07</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW7b</td>
<td>1M KCl</td>
<td>588-589</td>
<td>yes</td>
<td>1.71</td>
<td>0.005</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW7c</td>
<td>1M KCl</td>
<td>585-586</td>
<td>no</td>
<td>1.39</td>
<td>0.03</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW8a</td>
<td>1M CaCl2</td>
<td>NA</td>
<td>NA</td>
<td>1.49</td>
<td>0.02</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW8b</td>
<td>1M CaCl2</td>
<td>NA</td>
<td>NA</td>
<td>1.59</td>
<td>0.01</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW8c</td>
<td>1M CaCl2</td>
<td>585-586</td>
<td>no</td>
<td>1.15</td>
<td>0.05</td>
<td>weakly oxidised magnetite</td>
</tr>
</tbody>
</table>

*Table 4-3: Curie temperatures, Sextet ratio ($R$) and oxidation parameter ($x$) for the magnetites of the BMα set reacted with saline solutions. All the experiments yield weakly oxidised magnetites. Magnetic analysis on samples BMαW8a and BMαW8b were affected by a non-resolvable technical problem so this measurement was aborted. Sample BMαW2c presented a negative oxidation parameter due to excessive error during the spectroscopic analysis.*
The samples listed in Table 4.3 were all analysed within bentonite matrix during the Mössbauer analysis in order to evaluate possible Fe-enrichment of the clay matrix.

This led to an increased instrumental error and the evident discrepancy with the measured Curie temperatures of the magnetites, which systematically result higher than the respective $\chi$ if these results are compared to Table 4.1 and table 4.2.

The susceptibility analyses on these samples show that there is a different magnetic response to saline solutions and deionised water on one side and alkaline solutions on the other due to formation of a Fe$^{3+}$ spinel-structure phase ($\gamma$-Fe$_2$O$_3$).

4.6.3 BMαW6b and BMβW6b Sets – Time-dependent experiment

The samples from the BMαW6b ( uncompressed bentonite/magnetite) and BMβW6b ( compressed bentonite/magnetite) sets, reacted at 70°C, with one sample for each set extracted at intervals of one month over a total period of 5 months. The purpose of this set was to examine oxidation with time.

Figure 4-47: Susceptibility curves for samples of the BMαW6b and BMβW6b sets. The sample extracted after one month is on the left, whereas the one extracted after 5 months on the right. Heating curves are in red and cooling in blue. The black trace represents the second derivative of the cooling curve used to calculate the Curie temperature. Susceptibility measured in SI units and temperature in °C. b: non-sieved magnetite.
The susceptibility curves show the classic drop between 580 and 590°C as seen for the control samples of the Kirmag and BMα sets (Figure 4-47). No drop in susceptibility at around 350°C present.

As visible from Table 4-4, these samples feature different degrees of oxidation, but this is not consistently related to the duration of the experiment. The measured Curie temperatures do not register the higher degrees of oxidation of the samples (Figure 4-48), which should exhibit $T_C$ higher than 590°C, at $x > 0.2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Month</th>
<th>Solution chemistry</th>
<th>$T_C$ (°C)</th>
<th>R</th>
<th>$x$</th>
<th>Magnetic Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMαW6b</td>
<td>February</td>
<td>Mixed solution</td>
<td>587-588</td>
<td>0.3</td>
<td>0.21</td>
<td>oxidised magnetite</td>
</tr>
<tr>
<td>BMαW6b</td>
<td>March</td>
<td>Mixed solution</td>
<td>584-585</td>
<td>0.53</td>
<td>0.15</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>BMαW6b</td>
<td>April</td>
<td>Mixed solution</td>
<td>585-586</td>
<td>1.05</td>
<td>0.06</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMαW6b</td>
<td>May</td>
<td>Mixed solution</td>
<td>587-588</td>
<td>0.15</td>
<td>0.25</td>
<td>oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>June</td>
<td>Mixed solution</td>
<td>584-585</td>
<td>1.01</td>
<td>0.07</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>February</td>
<td>Mixed solution</td>
<td>586-587</td>
<td>0.2</td>
<td>0.24</td>
<td>oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>March</td>
<td>Mixed solution</td>
<td>584-585</td>
<td>0.61</td>
<td>0.14</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>April</td>
<td>Mixed solution</td>
<td>583-584</td>
<td>0.59</td>
<td>0.14</td>
<td>moderately oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>May</td>
<td>Mixed solution</td>
<td>585-587</td>
<td>0.82</td>
<td>0.1</td>
<td>weakly oxidised magnetite</td>
</tr>
<tr>
<td>BMβW6b</td>
<td>June</td>
<td>Mixed solution</td>
<td>583-584</td>
<td>1.02</td>
<td>0.07</td>
<td>weakly oxidised magnetite</td>
</tr>
</tbody>
</table>

*Table 4-4: Curie temperatures, Sextet ratio (R) and oxidation parameter ($x$) for the magnetites of the BMα set reacted with deionised water and alkaline solutions. Samples show different degrees of oxidation. For the composition of the mixed solution, refer to W6 in Table 3.2.*

*Figure 4-48: Oxidation parameter ($x$) vs. Curie Temperature ($T_C$) diagram for samples of BMαW6b and BMβW6b sets.*
4.6.4 Summary

The results on the samples of the Kirmag, BMα and BMαW6b and BMβW6b sets show that magnetites exhibit signs of oxidation, marked by increasing Curie temperature and corresponding oxidation parameter $x$ calculated from Mössbauer data.

These variations are not registered by the magnetic field generated by magnetite (a ferromagnetic mineral which generates an already weak magnetic field), unless the extent of oxidation causes formation of haematite, which is a canted antiferromagnetic phase that has not occurred in these experiments.

Magnetic susceptibility analysis on the samples reacted for five months with deionised water and saline solutions detected the presence of a secondary oxidation phase, a Fe$^{3+}$ spinel structure phase that was not found in any other sample. The samples from the time-dependent sets (BMαW6b and BMβW6b) exhibited an apparent trend with decreasing oxidation with time but this trend can be effected by instrumental error.

Considering these small changes were measurable only using very sensitive instruments and these levels of accuracy are not achievable in the field, where the environmental noise might make impossible to register such small variations, magnetite cannot be considered a suitable material for the remote monitoring of water saturation and fluid chemistry variations of an EBS in a Geological Disposal Facility.
4.7 Batch Experiments – Clay Matrix Evolution

Documentation of the evolution of the clay matrix is an important part of this study, particularly because it is critical to identify and/or characterise any possible corrosion-induced changes in clay mineralogy that might affect the mechanical properties of the bentonite buffer and have a negative impact on key parameters, such as suction power and swelling pressure.

In order to investigate this, the clay matrix was separated from the magnetic material through magnetic separation, or sampled within or outside the corrosion zone, chemically treated to digest the precipitated Fe oxyhydroxides [131], and then analysed following the guidelines from [146].

XRPD scan parameters and other information can be found in chapter 3.

In this section, the evolution of bentonite matrix in contact with each of the different magnetic materials used in this set of experiments is analysed.

Bentonite/magnetite samples were used to track the evolution of bentonite matrix (reacted with a saline solution with high pH) with time over a period of five months. This experiment was performed in order to determine whether, in a closed system with no fluid circulation, the mineralogical changes in the clay happen during the first reaction stages or throughout the experiment.

For the batch experiments, the research approach involved the study of the mineralogical changes occurring to the bentonite matrix mainly using the variations in the 001 reflection. Changes in the peak position from the starting material, as well as peak breadth and intensity, yield important information about cation exchange in the interlayer and/or Fe enrichment, and crystallization of Fe-bearing clays (chlorite/Fe-saponite/vermiculite).

Hence, in this chapter the 2θ range hosting the 001 reflection is shown in XRD traces in order to optimize the information provided and guarantee a better visualization of the changes occurring in peak position and width. The complete traces, classified according to experimental set and water chemistry are shown in appendices folder 4.6.
4.7.1 MX80 sodium bentonite

Figure 4-49: Oriented mount of the air-dried clay fraction of the unreacted MX80 sodium bentonite supplied by RS minerals. The 001 reflection is centred at 12.5Å and does not present pronounced shoulders.

The separated clay fraction of the initial unreacted MX80 bentonite (Figure 4-49) shows the typical pattern of a Na-montmorillonite, with a very sharp basal reflection centred at 7.1°2θ (equivalent to a d_{001} spacing of 12.5Å) and the rational sequence of 00l reflections. The accessory minerals fraction (Figure 4-50) shows a series of very narrow and distinctive peaks of several phases. Among these, the intense reflections of quartz (26.6°2θ), sanidine and albite (27-29°2θ) are observed. Less intense are the reflections of cristobalite, albite calcite and muscovite. The composition of the starting material is comparable to the MX80 bentonite studied by Madsen [147]. A low and broad reflection centred at 6.1°2θ (14.5Å) is related to the presence of a small amount of Ca-montmorillonite which was likely coating some of the grains of the accessory phases.
Figure 4-50: Random mount of the accessory minerals fraction of the unreacted MX80 sodium bentonite supplied by RS minerals. (Ms = muscovite, Qz = quartz, Ab = albite, Sa = sanidine, Cal = calcite).

The oriented MX80 sample (Figure 4-51) after glycol-solvation shows expansion of the d001 spacing to 17Å (ca. 5°2θ) and then collapse to 10Å (ca. 9.1°2θ) upon heating at 400°C with no further change after heating at 550°C.

Figure 4-51: XRPD traces of oriented mounts of MX80 sodium bentonite after glycol-solvation and heating at 400 and 550°C.
4.7.2 Control samples
As explained in detail in Chapter 3, a set of control samples was prepared in order to study the effects of the water composition on the bentonite matrix. Eight samples were prepared with the same solid/liquid ratio as the batch experiments and were reacted for 155 days at 70°C. Figure 4-52 shows the 2-10 2θ range for the XRPD traces of the control samples; all the traces show the standard behaviour of clays upon air-drying, glycol-solvation (expansion to ca. 17Å), and 400° and 550°C heating (collapse to ca. 10Å). However, significant variations in air-dried and 400°C-heated samples peak positions could be measured. These variations are used as reference values for the clay samples collected in the batch and fluid-flow experiments. The positions and shapes of the basal reflections are related to the cation exchange processes occurring in the clay interlayer. The shift of the AD (Air-dried) basal reflection for the samples treated with Ca-rich solutions towards lower diffraction angles (15Å for the CaCl₂ solution, close to the “typical” double water layer) is due to extensive Ca/Na cation exchange in the interlayer and formation of Ca-/Na-montmorillonite interstratifications [148]. Samples treated with K-rich solution feature AD basal reflections near 11Å [149] and expansion to ca. 17Å upon glycol-solvation, accompanied by peak broadening, which is well known for K-exchanged smectites [50]. The sample treated with NaOH solution shows a peculiar behaviour upon heating, with only partial collapse of the 001 reflection to 12Å. This may be due to the formation of random I/S interstratifications. The control sample treated with W6 (mixed saline solution with pH 11) featured significantly lower and broader basal reflections than the other specimens, accompanied by an increasing level of background noise. Given the complexity of the solution, this behaviour is considered to be related to K/Na and Ca/Na exchange in the interlayer and possible formation of interstratifications of Ca-Na/montmorillonites with K-exchange.

4.7.3 Magnetite/bentonite mixtures
The batch experiments involving magnetite/bentonite mixtures were divided into two sets. One set used a bulk crushed magnetite embedded in powdered (α) and one compressed (β) bentonite/mixture reacted with a W6 solution (extracted every month for five months). One other set used three different magnetite grain sizes embedded in bentonite and reacted with all the solutions and extracted after five months.
Figure 4.52: XRPD traces of MX80 Na-montmorillonite control samples. Samples reacted with Ca-rich solutions feature AD 001 peak shifted towards lower angles whereas K-rich solutions caused a shift towards higher angles. Samples treated with saline solutions show higher levels of noise. For the composition of W6, refer to Table 3.2.
Figure 4-53: XRPD traces of clay matrix of samples of BMb/α-β set (reacted with W6).
Figure 4-53 shows the 2-10 2θ range of the XRPD traces of the BMb/alpha-beta set. There is no evidence for any effect of compaction of the mixtures on the mineralogical changes, and no evidence for any a time-related change in cation exchange in the interlayer.

The set involving BMα(a-b-c) mixtures reacted with all the solutions does not show any differences related to the grain size of magnetites. Hence, for simplicity and ease of representation, only the 001 reflections of the clays collected from the BMcα (c > 120μm) mixtures are shown in Figure 4-54. Air-dried samples are centered at 12.5Å with tiny shifts due to limited cation substitutions in the interlayer. The only exceptions are the samples treated with KCl- and CaCl₂-solutions, which feature basal reflections centered at 11.3 and 15Å respectively. Upon glycol-solvation, all specimens show expansion towards ca. 17Å, with minimal differences from the sample reacted with deionised water. Hence, the differences in the AD basal spacing could be attributed to K/Na and Ca/Na substitution in the interlayer. After heating, all specimens show collapse of basal reflection to 10Å, with the exception of the sample treated with NaOH solution (partial collapse to 12Å, indicating the likely formation of random I/S interstratifications) and the KCl-solution treated sample (001 peak centered at slightly lower 2θ angle than the other samples after heating at either 400 or 550°C).

The specimen treated with W6 features very low and broad basal reflections with respect to the other samples; this is considered to be due to Ca+K/Na exchange and a smaller crystallite size of the clay particles. The cation exchange, in this case, may have caused formation of both K-exchanged montmorillonites and interstratified Ca/Na montmorillonites or a highly disordered cation substitution in the interlayer. This might explain why the neither the typical “double water layer” at 15.4Å [150] for Ca-montmorillonite nor the basal peak at 11Å for the K-exchanged montmorillonites are visible. Air-dried peaks are normally centered around 12.5-13Å for all the samples and the tiny variations that could be measured are due to the high chemical heterogeneity of these samples, resulting from minor but inhomogeneous cation exchange throughout the specimen.
Figure 4.54: XRPD traces of Air-dried, glycol-solvated, 400° and 550°C heated clay specimens from set BMca. Lines with the same colour belong to the same sample. For the composition of W6, refer to Table 3.2.
4.7.4 Synthetic magnets/bentonite mixtures
As seen in the pictures of the reaction vessels taken straight after the extraction from the oven in the previous subchapters, the clay specimens did not have any presence of reaction haloes around the magnet fragments in all the ferrite/bentonite samples (Figure 4-33) and in most of the samples reacted with alkaline solutions (Figure 4-1 and Figure 4-27).

Some of the clay specimens in contact with SmCo or AlNiCo magnets (Figure 4-21 and Figure 4-28) and reacted with saline waters showed pale red coloured haloes at the water/clay interface, marking a likely Fe-oxyhydroxides precipitation volume.

In the samples in which Nd-Fe-B magnets were reacted, the clays appeared substantially unaltered, even when reacted with deionised water and alkaline solutions (Figure 4-1), and despite the obvious precipitation of Nd and Fe oxyhydroxides at the magnets/clay interface. In the Nd-Fe-B samples reacted with saline solutions (Figure 4-3 and Figure 4-4), two main domains could be defined within the matrix. The first domain (reaction zone), located at the boundary between the clay matrix and the magnetic fragments, is characterised by black oxyhydroxide precipitated and a red halo at the bentonite-water interface, fading into a yellow to greenish-grey color towards the bentonite matrix. This domain is inferred to reflect the precipitation of Fe oxyhydroxides during aerobic corrosion. The second matrix domain, outside the reaction zone, is unchanged. Three samples were taken in both domains.

In case where oxides/oxyhydroxides were present in the analysed domains, they were digested by sodium dithionite - sodium citrate system buffered with sodium bicarbonate [131].

Here, the results are divided into four sections according by the type of magnet used in the experiment. For synthetic magnet/bentonite mixtures only the 001 reflections peaks for the four stages of clay analysis (AD, glycol-solvated and heating at 400°C and 550°C) are reported. The complete traces are shown in appendices 4.6.4 1/2/3/4.
4.7.4.1 **Ferrite/bentonite**

The matrix in the Ferrite+bentonite set appeared unchanged in all the specimens and no signs of corrosion-related alteration of clays were detected even during cleaning of the magnetic fragments.

The analysis of the position of the clay basal reflections in the Air-dried and glycol-solvated XRPD traces (Figure 4-55) shows the same behaviour described for the control samples and the BMα/βW6b set. Samples reacted with KCl CaCl₂ solutions showed reflections considerably lower in intensity than the other samples, with the glycol-solvated traces showing almost a flat profile. As shown in Appendix 4.6.4.1, the complete XRPD traces of KCl- and CaCl₂- treated samples show noisy traces, with a pronounced hump indicative of the presence of amorphous silica in the glycol-solvated CaCl₂ trace. This interesting feature may be interpreted as related to dissolution/reprecipitation of sheet-silicates, which could be a precursor of formation of random/ordered interstratifications of Ca/Na-montmorillonites or random I/S.

![Figure 4-55: XRPD traces of Air-dried and glycol-solvated clay specimens from Ferrite+bentonite set. Lines with the same colour belong to the same specimen.](image-url)
Upon heating at 400°C, all Ferrite+bentonite set clay samples feature a clear collapse of the basal reflection to 10Å, with no further collapse after heating at 550°C (Figure 4-56). The only specimen to feature a consistent difference from the control sample is the 400°C-heated NaOH-treated specimen, which records complete collapse rather than partial collapse, although the left shoulder is wide and well-pronounced.

4.7.4.2 AlNiCo/bentonite
The clay matrix in these samples did not exhibit intense corrosion-related changes in colour, apart from some haloes formed by precipitation of oxyhydroxides (Figure 4-28). Similarly, to the samples from the Ferrite+bentonite set, XRPD traces for these samples show positions of the 001 basal reflections comparable to the control samples (Figure 4-57). Specimens treated with KCl- and CaCl2- rich solutions exhibit noisy traces with a relatively high background, suggesting that they may have been affected by dissolution/reprecipitation processes.
Figure 4-57: XRPD traces of Air-dried, glycol-solvated, 400°C and 550°C heated clay specimens from set AlNico+bentonite. Lines with the same colour belong to the same specimen.
4.7.4.3 *SmCo/Bentonite*

Samples reacted with saline solutions and deionised water featured significant traces of corrosion-related products at the magnet/bentonite interface, such as precipitation of oxides and oxyhydroxides. Furthermore, the matrix itself was characterised by the presence of a shaded halo around the magnets, with a range of colours fading from an olive green adjacent to the SmCo magnets to a very light yellow/grey towards the matrix.

In contrast to the samples of Ferrite+bentonite and AlNiCo+bentonite sets, the AD basal reflections in these experiments show that differ considerably from those of the control samples. The shapes of the 001 peaks of the AD clays (Figure 4-58 – left) are broad and asymmetric, consistently with random mixtures of clays. Furthermore, the peak intensities are significantly lower in the saline solution reacted clays. The complete traces (Appendix 4.6.4.3) feature high noise and elevated background in the samples reacted with saline solutions, consistent with presence of high amounts of amorphous or microcrystalline domains.

![Figure 4-58: XRPD traces of Air-dried and glycol-solvated clay specimens from SmCo+bentonite set. Lines with the same colour belong to the same specimen.](image-url)
The samples reacted with Ca-rich solutions feature 001 reflections centered at 5.6°2θ (14.9Å), which shifts to 5.2°2θ (17Å) after glycol-solvation. Upon heating, the peaks shift towards 10Å; this behaviour is consistent with a Ca-montmorillonite being the dominant clay in the sample. The pronounced shoulders at lower 2θ angle in the AD traces suggest possible presence of vermiculite.

Samples reacted in deionised water and NaCl-solution feature a 001 peak in the AD trace (Figure 4-58) centered at 5.9°2θ (15Å) shifting to 5.2°2θ (17Å) after glycol-solvation. Considering that these two samples did not have any calcium in solution, this behaviour interpreted to reflect the presence of dioctahedral vermiculite (Fe³⁺-rich) or trioctahedral vermiculite (Fe²⁺-rich). Upon heating at 400°C (Figure 4-59) the sample reacted with NaCl solution shows collapse of the 001 reflection to 7.3°2θ (12.1Å) with another peak at 9.1°2θ, collapsing further to 9°2θ (9.8Å) after heating at 550°C. This behaviour is consistent to the presence of either di- or trioctahedral vermiculite.

![Figure 4-59: XRPD traces of 400°C and 550°C-heated clay specimens from SmCo+bentonite set. Lines with the same colour belong to the same specimen.](image)
The sample reacted with deionised water, unlike the NaCl one, features collapse to 10 Å after 400°C heating with no further change after 550°C heating. This peculiar behaviour is consistent with presence of trioctahedral vermiculite or nontronite.

Samples reacted with NaOH and KOH solutions show an intense and asymmetric (pronounced left shoulder) 001 AD reflection centered at 7°2θ (12.45 Å) shifting towards 5.2°2θ (17 Å) after glycol-solvation. After heating (Figure 4-59) the two samples display the same behaviour as the control samples (Figure 4-52).

The sample reacted with KCl solution (Figure 4-58 and Figure 4-59) features 001 reflections much weaker than the other clay samples and traces characterised by high levels of noise. The 001 peak shows the same behaviour as the respective control sample (Figure 4-52).

The clay matrix collected in the samples of the SmCo+bentonite set shows presence of Fe-rich vermiculite together with Na-montmorillonite in the samples reacted with saline solutions and deionised water. The samples reacted with alkaline solutions show a behaviour similar to the control sample but presence of vermiculite or interstratified montmorillonite/vermiculite material cannot be excluded in the sample reacted with Ca(OH)₂ solution, which shows asymmetry of the AD basal reflection.

Hence, the changes arising within the clay matrix in the SmCo+bentonite set experiments mainly reflect the formation of random mixtures of clays. These changes are partly due to the initial solution composition and partly to the corrosion of the magnetic alloy and availability of Fe in the system.

4.7.4.4 Nd-Fe-B/bentonite

Nd-Fe-B sample reacted with deionized water showed disaggregation of the magnets, but did not feature any reddish halo in the clay matrix. Samples reacted in alkaline environments showed only partial oxidation of the magnets, with formation of a layer of oxyhydroxides (Nd(OH)₃ and FeOOH) on the magnet surfaces, as confirmed by X-ray semi-quantitative analysis. The formation of these oxides and oxyhydroxides has been discussed in Section 4.2.

The XRPD patterns of air-dried and glycol-solvated clays collected from the deionized water-treated sample show the series of basal reflections characteristic of Na-
montmorillonite, and thus shift towards lower diffraction angles after glycol-solvation (Figure 4-60).

The XRPD traces of the air-dried samples after reaction with alkaline solutions (Figure 4-60) show slightly asymmetric 001 reflections centered at 12.6 Å for the bentonites reacted in NaOH solution. The KOH-solution treated sample shows a peak centered at a slightly higher diffraction angle. The Ca(OH)₂-solution reacted bentonite shows a weaker and broader basal 001 reflection centered at 14.2° 20. All the traces collected after glycol-solvation show a shift of the first basal reflection towards lower diffraction angles (corresponding to 17.0 Å d-value) and sharpening of the peaks.

![Figure 4-60: XRPD traces of air-dried and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures.](image)

The different behavior of the air-dried Ca(OH)₂-solution treated sample with respect to the others is explained once again by the formation of interstratified Ca-Na-montmorillonite in this solution [148].

The clays collected at the magnet/matrix interface in the samples reacted in saline solutions showed very weak or flat reflections (Figure 4-61). The air-dried pattern
shows peak intensities 20 times lower than the samples showed in Figure 4-60 and Figure 4-62.

Glycol-solvated samples in the saline set show slightly more intense and sharper 001 reflections, but these are still rather low in comparison, for example, to samples treated in alkaline solution (Figure 4-60). The traces without background removal show a hump typical of amorphous silicates. After heating at 400°C and 550°C the basal reflections collapse to 10Å (Appendix 4.6.4.4)

![Figure 4-61: XRPD traces of air-dry and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures and sampled at the magnet/matrix interface. The traces were all smoothed and the background removed. All the 001 reflections result very small and broad peaks (Air-dried KCl-solution trace is flat) that slightly increase in intensity and shift towards lower diffraction angles after glycol-solvation.](image)

The clays sampled in the matrix unaffected by magnet corrosion or availability of Fe (Figure 4-62) showed XRPD traces with the rational series of basal reflections. KCl- and CaCl₂-solution treated samples displayed a significantly decreased basal reflection in the air-dried traces compared to the NaCl-solution reacted sample. The glycol-solvated traces (Figure 4-62) show expansion of the d₀₀₁ to 16.8Å. The KCl-treated sample has a broad peak after glycol-solvation.
The clays collected at the magnet–matrix interface in the samples showing the most intense effects of corrosion, displayed very weak and broad basal reflections even after glycol solvation. These weak and broad reflections are thought to be related to a low-temperature dissolution/reprecipitation that results in the formation of nanoparticulate interstratified clays. Broad weak maxima are produced by the combination of fine particle size and poor crystallinity with complex random interstratification (as found in soil profiles by Brown & Jackson [151]). These interface-controlled clays, formed within a silica gel matrix, might represent a step in the evolution of pure Na-montmorillonite towards a Fe-enriched member.

Figure 4-62: XRPD traces of air-dry and glycol-solvated clays from Na-montmorillonite/Nd-Fe-B mixtures and sampled in the unaltered matrix. The positions of 001 reflections in the air-dry traces of KCl- and NaCl-solution treated samples show significant deviation from the CaCl2-water treated sample but they all centered at 16.8Å after glycol-solvation.
4.7.5 Summary of clay behavior

XRPD analysis performed on oriented mounts on the clays extracted from the batch experiments showed behaviors in line with the control samples, with shifts of the 001 basal reflection essentially controlled by Ca/Na and K/Na exchange in the interlayer for the samples from Ferrite+bentonite, AlNiCo+bentonite and NdFeB+bentonite sets. This causes formation of K-exchanged montmorillonites and interstratified Ca-/Na-montmorillonites, characterized respectively by a shift towards higher and lower diffraction angles in the air-dried traces. The samples characterized by the most evident traces of corrosion featured very noisy traces with high background humps due to formation of amorphous silicates. Traces of Fe-bearing clays (in particular the presence of dioctahedral or trioctahedral vermiculite) were only detected in some samples of the SmCo+bentonite set. Nevertheless, the presence of Fe-bearing amorphous silicates in the reaction haloes of the samples showing the most intense corrosion effects cannot be excluded.

All clay samples featured expansion of the d-spacing to ca. 17Å upon glycol-solvation so it can be concluded that the transformations occurring in the matrix do not significantly affect the clay swelling properties.

Hence, it can be confirmed that most of the changes occurring to the bentonite matrix are related to the initial solution composition and that magnet corrosion itself does not lead to any significant loss of performance of the matrix in terms of swelling capacity. This positive result arises because the corrosion-related, neoformed Fe-bearing clays have equivalent swelling properties to the initial material.

In summary, the 70°C batch experiments performed in this study demonstrate that the corrosion of synthetic magnets has little or no negative impact on the bentonite performance.
4.8 Batch Experiments - Solution chemistry
In the batch experiments run in sealed bottles with no reactants recharge and free pH drift, dramatic changes in solution chemistry are expected, especially with respect to the concentrations of metals in solution due to the corrosion of the magnets. Silicon (Si) concentrations have been measured but are not displayed because they might be affected by the chemical alteration of the borosilicate glass. Errors on the quantification of the abundance of the single elements are within the range of ±10% relative to each element.

The ICP-OES results show dramatic changes in the fluids reacted with synthetic magnets/bentonite mixtures clearly related to the initial solution pH or salinity.

The fluids from NdFeB+bentonite set show very low concentrations of Nd, consistent with the immediate precipitation of Nd hydroxides or hydrides at the magnet/clay interface. The concentrations of Sr, Fe and Al appear to be related to the initial solution chemistry. Aluminium reaches very high concentrations in the high pH solutions and deionized water-treated samples, and this could be related to dissolution of the bentonite matrix. Boron reaches high concentrations in the CaCl₂ solution treated sample; however, its concentration may be affected by the corrosion of the borosilicate glass. The high concentrations of Sr in all sets are restricted to the saline solutions, and to the impurities present in the reagents used to prepare the solutions.

![Figure 4-63: Metal ions in solution in bentonite porewater in the samples of NdFeB+bentonite set.](image-url)
Figure 4-64: Metal ions in solution in bentonite porewater in the samples of AlNiCo+bentonite set.

Samples of the AlNiCo+bentonite set (Figure 4-64) display different behaviour compared to the NdFeB+bentonite set (Figure 4-63). Co and Fe show high concentrations in saline solutions, consistent with the observed higher magnet corrosion effects observed in those samples. Boron concentrations follow the same pattern observed for samples from the NbB set, although the concentrations are lower. Interestingly, these samples feature very low concentrations of Al in solution, despite the AlNiCo alloy contains up to 13% of Al. This low concentration could be caused
by the precipitation of Al oxyhydroxides to accommodate the Al produced either by corrosion of the magnet or dissolution of bentonite.

Samples from the SmCo+bentonite set (Figure 4-65) have higher concentrations of Sm, Fe and Co in saline solutions, as previously observed for AlNiCo+bentonite set, and slightly higher concentrations of Al in alkaline solutions. Boron concentrations follow the same trend as seen for AlNiCo+bentonite set samples.

Samples from the Ferrite+bentonite set (Figure 4-66) exhibit very high concentrations of Sr in saline solutions. Boron follows the same trend seen in samples from AlNiCo+bentonite and SmCo+bentonite sets. Al shows a distinct spike in the 0.1M NaOH solution treated sample.

These results on the changes in fluid composition agree with the observed corrosion effects on the samples and with the results of XRPD analysis on clays and magnets. Given the intrinsic chemical complexity of this kind of batch experiment, only basic observations can be made on the different behaviours of transition metals in solution between the four mixtures.

![Bentonite porewater (FeB set)](image)

*Figure 4-66: Metal ions in solution in bentonite porewater in the samples of Ferrite+bentonite set.*

Samples of NdFeB+bentonite set feature higher transition metals concentration in alkaline solutions and deionized water than samples in AlNiCo+bentonite and
SmCo+bentonit set, whereas for the saline solutions the situation is reversed. This difference might be explained with the fact that these batch systems are chemically identical only at the start of the experiments but then they evolve in different ways. Considering that pH, oxygen saturation and hydrogen pressure can change dramatically from one sample to the other within the same set, these changes are likely to be greater between sets in which two different alloys have been corroded. These shifts in bulk properties might have caused precipitation of Fe oxides and oxyhydroxides in saline environments in the NdFeB+bentonite sets, with the solutions consequently being depleted in Fe. On the other hand, in the alkaline environments, the chemical conditions might have not been favourable for the precipitation of Fe oxides and oxyhydroxides, with the solutions consequently enriched in Fe.

4.9 Batch Experiments - Concluding remarks

The batch experiments had the purpose to test the reactivity of selected natural and synthetic magnets under “extreme” solution compositions, which are not expected to be found in a time-evolved underground repository for Nuclear Waste. The purpose was to understand whether they could be good candidates as sensors for groundwater chemistry variations.

From these simple experiments, it is evident that it is possible to detect water saturation in the Clay Barrier System through the variations of the magnetic field generated by the corroding magnets embedded in the clay matrix.

The magnetic characterisation of the samples (Hysteresis analysis, Curie point analysis) shows clearly that Nd-Fe-B and SmCo permanent magnets react with all solutions, leading to clear and measurable changes in the laboratory. AlNiCo showed smaller changes that are nevertheless still measurable. Hence, these three materials are believed to be capable of producing magnetic field changes that are measurable even with distant magnetometers because of their very high initial magnetic fields.

Ferrite, despite having an initially very strong magnetic field, did not show any change of magnetic properties on the timescale of these experiments. This suggests that cannot be considered as a suitable material for magnetic monitoring of water saturation and fluid chemistry variations of the Engineered Barrier System. However, given its high magnetic field and lack of reactivity, it may be useful for providing an enhanced long-
lived background signal to reduce the effects of magnetic noise from the surrounding geosphere.

Magnetite, considering its much lower intensity magnetic field and low reactivity even under “extreme” environmental conditions, cannot be considered suitable for the purpose of this project.

The analysis of the clay matrix shows changes mainly related to the initial composition of the solution, with the formation of Ca-montmorillonite or K-exchanged montmorillonite arising from Ca- and K-rich solutions respectively. However, Fe enrichment of the clay matrix in the surroundings of the magnets is not excluded by these experiments and in the samples from the SmCo+bentonite set some vermiculite or interstratified vermiculite/montmorillonite material has been identified. Fe enrichment of the bentonite matrix did not cause formation of non-swelling materials (like Chlorite) under the conditions investigated.
5 Results of Confined Fluid Experiments

5.1 Introduction

This data chapter represents the refinement of the batch experiments, in which the applied conditions were more controlled and closer to a real “evolved” EBS. In these experiments, the magnetic materials retained after assessment of the Batch experiments have been embedded within bentonite matrix in experiments designed to have confined swelling and imposed fluid flow.

The design of this experiment is specifically aimed to react the magnets in one environment characterized by continuous supply of reactants and stable boundary conditions (pH at the filter/bentonite interface around 12) under dysoxic conditions. The solution used was a 0.273M NaCl solution reacted with NRVB cement to increase its pH to 12, and purged with N₂ gas, to simulate a solution in a subsurface alkaline plume interacting with the EBS. Three stacks of reaction vessels were prepared and extracted at intervals of 4 months to study the evolution of the magnetic system with time. Hence, these experiments allow analysing the long-term evolution and behaviour of the magnets that have been shortlisted after the Batch experiments.

An important target of these experiments is the identification of corrosion-related, non-swelling clays and their differentiation from the matrix/cement porewater interaction products. This study is essential in order to understand and assess the impact of this passive monitoring technique on the stability of the bentonite buffer.

More information on the design of the experiment are present in section 3.3, whereas the information on the analytical techniques in section 3.5. The complete XRPD traces of clays are presented in appendices folder 5.4. Tables with a summary of the results are presented at the end of section 5.6.
5.2 Confined Fluid Flow Experiments – Nd-Fe-B permanent magnets
This section shows the results of the XRPD and magnetic analysis on both the uncoated Nd-Fe-B magnets and the coated Nd-Fe-B magnets.

At the time of the extraction, the coated Nd-Fe-B magnets were intact in all samples, showing oxidation of the outer Co coating (likely cobalt oxides) and precipitation of orange-coloured materials (probably Cu-bearing phases produced by the corrosion of the inner Cu layer of the coating). Considering the extremely small amount of oxidation material available and the technical difficulty to perform a chemical (EPMA or SEM analysis) on permanent magnetic materials, these phases are regarded being Co oxides and Cu-bearing phases based on the chemistry of the oxidised noble metals composing the coating.

XRPD traces of the corroded coated Nd-Fe-B magnets all show clear and sharp reflections of the main magnetic phase (Figure 5-1); these are only weakly shifted towards lower diffraction angles with respect to the unreacted Nd-Fe-B magnet.

![Figure 5-1: XRPD traces of the coated Nd-Fe-B magnets extracted from Stacks 3A, 3B and 1 (from bottom to top) compared with the raw Nd-Fe-B alloy. Peaks of the main magnetic phase in the corroded magnets are slightly shifted towards lower diffraction angles (red dashed lines).](image-url)
Figure 5-2: XRPD traces of the uncoated Nd-Fe-B magnets extracted from stacks 3A, 3B and 1 (from bottom to top) compared with the raw Nd-Fe-B alloy. Peaks of the main magnetic phase in the corroded magnets are shifted towards lower diffraction angles (red dashed lines).

At the time of the extraction, the uncoated Nd-Fe-B magnets were still intact in all samples, but evident traces of corrosion were visible. The magnets were extremely fragile and they disaggregated steadily at the act of the separation from the matrix.

XRPD traces of the corroded uncoated Nd-Fe-B magnets show different characteristics in each of the three stacks. Sharper and more intense reflections are seen, at the same 2θ angles, in the longest duration experiment sample. This may result from better crystallization of Nd-Fe-B hydrides in the longest duration sample or from presence of random mixtures of poorly crystallized Nd-Fe-B hydrides in the other two samples.

The results of the XRPD semi-quantitative analysis (Figure 5-3) show clearly the differences between the coated and uncoated Nd-Fe-B samples. The former are constituted by mixture of Nd-Fe-B hydrides in different amounts, and the latter are mainly composed by non-reacted Nd-Fe-B alloy with subordinate mixed hydrides.
Figure 5-3: Pie charts showing the composition (normalized to 100%), in terms of Nd-Fe-B hydrides, of the uncoated Nd-Fe-B magnets (left column) and of the coated Nd-Fe-B magnets (right column). These pie charts consider the main magnetic phases only.
Figure 5-4: Hysteresis loop of the raw Nd-Fe-B magnet (A) and of the coated Nd-Fe-B magnets extracted after 4 months (B), 8 months (C) and 12 months (D). The red dashed lines in (B) and (D) represent the magnetization curve.

The hysteresis loop obtained on the reacted coated Nd-Fe-B magnets exhibit evidence that the corrosion took place. After 4 and 8 months (Figure 5-4 B and C) the samples show an indentation of the hysteresis loop and a decrease of the remanence from 145.3 Am²/kg in the raw material to 84 Am²/kg and 117.5 Am²/kg in Sample 3A and 3B respectively. The reacted samples show the same coercivity value of the raw sample of 1.2T. The sample from Stack 1 reacted for 1 year (Figure 5-4D) not only features an even more pronounced indentation of the hysteresis loop at low applied field (giving a remanence of 65.8 Am²/kg) but also has a considerably lower coercive field at 0.61T.
Samples from Stacks 3A and 3B also show presence of a second hard ferromagnetic phase with coercive field of 0.82T. The decrease in remanence is indicative of a decreasing percentage of the hard phase that is non-compensated by the presence of neo-formed soft phases. In this case, the lower remanence is explained by presence of non-ferromagnetic materials.

The transition from a square-like ferromagnetic loop to the pot-bellied loop (after 4 and 8 months) remarks the antiferromagnetic coupling of the initial ferromagnetic, high-coercivity and small switching field distribution phase with a low-coercivity, high switching field distribution, corrosion related secondary ferromagnetic phase [152]. The transition to a wasp-waist loop after 12 months is indicative of coupling of two ferromagnetic materials with different coercivity [153] (the initial hard φ-phase and a corrosion-related softer ferromagnetic Nd-Fe-B hydride).

The uncoated Nd-Fe-B samples feature a behaviour similar to the samples of the batch experiments with a dramatic change of the hysteretic parameters. The sample extracted after 4 months (Figure 5-5B) exhibits very low coercivity at 0.1T and remanence at 12.9 Am²/kg. The other two samples (Figure 5-5 C and D) show a hysteretic behaviour typical of a superparamagnetic material with the disappearance of the squared loop and no coercive field or remanence; this transition is consistent with the formation of a complex mixture of soft magnetic phases and paramagnetic phases.

The coated samples show a time-dependent evolution of the hysteretic properties coherent with formation of soft magnetic phases after the preferential corrosion of the interstitial ρ-phase and initial formation of structural defects on the grains of the main magnetic phase (φ-phase), followed by the formation of a secondary hard magnetic phase, likely a Nd-Fe-B hydride and precipitation of non-ferromagnetic phases.

The uncoated samples show a less clear time-dependent evolution, due to the fact that the hysteretic properties are already completely lost after 8 months and even after 4 months either remanence or coercivity were very close to zero, after having lost more than 90% of the initial value.

The uncoated samples feature a sharp transition from a high-coercivity single-domain loop of the raw N42 Nd-Fe-B to the superparamagnetic loops of the samples reacted
for more than 4 months, with zero coercive field and remanence. The sample reacted for four months feature a wasp-bellied loop, with very low coercivity and remanence; the frequent indentations of the loop, suggest that this sample might have a complex mineralogy of the ferromagnetic component, with more than one phase, typically two coupled ferromagnetic phases with different coercivity [154]. In these samples, however, the contribution from mixed grain sizes may play a considerable role together with the mineralogy.

Figure 5-5: Hysteresis loop of the raw Nd-Fe-B magnet (A) and of the uncoated Nd-Fe-B magnets extracted after 4 months (B), 8 months (C) and 12 months (D). The red dashed lines in (B), (C) and (D) represent the magnetization curve.
The thermomagnetic analysis of the coated Nd-Fe-B samples (Figure 5-6) shows complex profiles with a main drop in magnetization at 300-350°C and another around 790°C. The samples reacted for four and eight months (Figure 5-6 B and C) show a heating curve with a double drop in the area 300-350°C, with one Curie temperature at 311°C and one at 330°C. Both these drops maintain the same height of the initial raw N42 Nd-Fe-B magnet, so there is no apparent decrease in the proportion of the main magnetic phase. The double drop at 310 and 330°C is consistent with the presence of two main magnetic phases, the original Nd$_2$Fe$_{14}$B and the hydride (Nd$_2$Fe$_{14}$BH$_{1-2}$). However, the cooling curve exhibits only one Curie point at 310°C, indicating that an irreversible transformation happens to the Nd-Fe-B hydride upon heating.

The sample reacted for 12 months (Figure 5-6D) exhibits only one step at 350°C, consistent with an Nd-Fe-B hydride with an overall higher number of hydrogens per unit formula. The heating curve features a slightly lower drop at 350°C than the raw sample at 310°C, indicating that, after heating, a lesser amount of the main magnetic phase is maintained. This hydride also shows an irreversible transformation upon heating, with the cooling curve showing only one Curie point at 310°C.

The thermomagnetic analyses of the uncoated magnets were affected by several problems. One sample holder (uncoated Nd-Fe-B – Stack 3A) exploded in the furnace (at approximately 340°C). This is considered to reflect the release, upon heating, of high quantities of hydrogen gas. The other sample (uncoated Nd-Fe-B – Stack 1) exhibited negative signal values, which indicate that the material has lost its thermomagnetic properties.
Figure 5-6: Thermomagnetic curves of the raw N42 Nd-Fe-B permanent magnet (A) and of the coated Nd-Fe-B magnets extracted after 4 (B), 8 (C) and 12 months (D). The black lines indicate Curie points of the magnetic phases.
In Figure 5-7B it is visible how little the drop in signal due to the main magnetic phase has become and how high the Curie temperature has risen in comparison to the initial material. Again, the behaviour of the cooling curve indicates that the Nd-Fe-B hydride (Nd$_2$Fe$_{14}$BH$_3$) is unstable at high temperatures.

The heating curves of all the reacted samples (coated and uncoated) feature a rising magnetization after 400°C and a fall at approximately 790°C. This is consistent with the formation of Fe(0) upon heating caused by decomposition of metastable phases such as Fe (oxy)hydroxides or metastable (upon heating) Nd-Fe-B hydrides.
5.3 Confined Fluid Flow Experiments - SmCo permanent magnets

After their extraction, the SmCo magnets showed oxidised surfaces and a presence of orange/coloured precipitates (likely Cu-bearing minerals). The discs were still intact and no exfoliation was detected, although some of the discs exhibited small fractures.

\begin{figure}
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\caption{SmCo26 raw}
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\includegraphics[width=\textwidth]{SmCo_stack_3A}
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\includegraphics[width=\textwidth]{SmCo_stack_3B}
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\begin{subfigure}{0.45\textwidth}
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\includegraphics[width=\textwidth]{SmCo_stack_1}
\caption{SmCo - Stack 1}
\end{subfigure}
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4 months

5 months

12 months

Figure 5-8: Hysteresis loops of the unreacted SmCo magnet (A) and of the SmCo magnets reacted for 4 (B), 5 (aborted sample, C) and 12 months (D). Green circles show areas where the hysteresis loop shows some steps due to presence of “soft” magnetic phases, and the red circle an indentation of the hysteresis loop marking the presence of a secondary “hard” magnetic phase.
The hysteresis loops of the reacted SmCo magnets feature very interesting characteristics (Figure 5-8). The samples extracted after 4 (Figure 5-8B) and 5 months (Figure 5-8C) show identical loops. With respect to the raw sample (Figure 5-8A) these two samples show some indentation of the hysteresis loop in the areas circled in green, at very low applied fields. These indentations are related to the presence of phases with low coercive fields (“soft” ferromagnets).

Saturation magnetization and remanence are constant for all samples at 102.3 Am^2/kg and 99 Am^2/kg respectively. The sample reacted for 12 months (Figure 5-8D) exhibits a small indentation of the hysteresis loop, corresponding to a coercive field of 2.3T, significantly smaller than the coercive field calculated at 2.85T.

The thermomagnetic curve of the unreacted SmCo26 (Figure 5-9A) permanent magnet shows a clear drop in magnetization at 825°C, typical for a standard SmCo magnet of the Sm2Co17 family.

The reacted SmCo magnets (Figure 5-9B, C, D) exhibit completely different heating curve patterns, with an initial increase of the magnetization until a first drop is achieved at 825°C and a second drop at 960°C or 930°C.

The comparison of the heating curves in the 50-800°C range indicates that the corrosion may have affected the thermomagnetic behaviour of the main magnetic phase through the formation of structural defects affecting the magnetic domains.

A Curie temperature of 930-960°C does not correspond to the most common corrosion by-products magnetite (580°C), iron (769°C) or cobalt (1126°C) nor to the T_Cs of the SmCo oxidation phases listed in chapter 2.3.1. The phases characterised by these high Curie temperatures may be metastable, as suggested by the cooling curves of the reacted samples, which display an irreversible behaviour with increasing magnetization between 895°C and 903°C. One possible explanation for this behaviour is that the corrosion process led to the formation of a significant amount of a soft magnetic phase with a Fe-Co composition. However, a metastable, oxidised, near-equiatomic Fe-Co corrosion-related phase [155] [156] with defect containing structure does not explain an increasing coercivity of the corroded alloy and unchanged intrinsic magnetic properties.
Figure 5-9: Thermomagnetic curves of the SmCo permanent magnets extracted after 4 (B), 5 (C) and 12 months (D) and of the initial SmCo26 permanent magnet (A). Vertical axes represent the signal percentage in comparison to the magnetization saturation of the sample.

Based on the data available, the identification of this secondary, corrosion-related phase resulted a non-trivial case. A similar magnetic behaviour was observed by Isnard et al. [157] and an increase of Tc upon insertion of H, N or C in R2M17 (R = Rare Earth Element, M = transition metal) was observed by Kianvash & Harris [158], Gubbens et al. [159], Kou et al. [160] and Sun et al. [161]. Hence, this corrosion-
related ferromagnetic phase is consistent with the presence of a hydrogen-decrepitated Sm$_2$Fe$_{17}$-type phase together with the starting Sm$_2$(Fe, Co, Cu)$_{17}$ magnetic phase.

5.4 Confined Fluid Flow Experiments - AlNiCo permanent magnets
At the time of extraction, all AlNiCo samples exhibited lose evident traces of corrosion, with areas characterised by dark-coloured stains (likely areas of localised pitting corrosion) and precipitation of neo-formed oxides or (oxy)hydroxides.

Figure 5-10: Hysteresis loops of the unreacted AlNiCo magnet (A) and of the AlNiCo magnets reacted for 4 (B), 8 (C) and 12 months (D). The red dashed lines represent the magnetization curve.
The hysteresis analysis (Figure 5-10) reveals that the AlNiCo magnets do not exhibit considerable variations of the hysteretic properties, with the coercive field at 0.065 T for all samples and remanence varying from 44.8 Am²/kg in the raw AlNiCo5 to 40.8 Am²/kg for the AlNiCo – Stack 3A. Saturation magnetization varies between 163 and 153 Am²/kg.

Figure 5-11: Thermomagnetic curves of the AlNiCo permanent magnets extracted after 4 (B), 8 (C) and 12 months (D) and of the initial AlNiCo permanent magnet (A). Vertical axes represent the signal percentage in comparison to the magnetization saturation of the sample. Increasing magnetization of the cooling curves is explained by stress relaxation post-heating.
The thermomagnetic analyses (Figure 5-11) on the run AlNiCo samples confirm the outcome of the previous hysteresis analysis. No traces of corrosion-related phases were detected and the Curie temperature of the alloy is at 860°C for all samples. The increasing magnetization of all the cooling curves with respect to the heating curves is explained by the effect of stress relaxation after heating.

Hence, the AlNiCo magnets did not feature any significant corrosion-related change of hysteretic and thermomagnetic properties under the conditions investigated here. The only difference measured on the remanence values, of some -5% from the raw material, suggests that the corrosion-driven changes in magnetic field would not be measurable in the field unless extremely sensitive magnetometers are used.

### 5.5 Confined Fluid Flow Experiments - Clay matrix

The bentonite matrix samples extracted from the confined-fluid flow experiments presented a layered structure, with a thin encrusted layer (or domain) at the interface with the sinter glass disc and a soft layer at the bottom (see Figure 5-16). The two layers were analysed separately in their clay (<2μm) and coarse fractions (>20μm) because the accessory minerals are believed to play a major role in the evolution of the bentonite matrix.

The non-separated matrix was analysed with random powder mounts using pure reagent grade zincite as internal standard. Separated coarse material was analysed on random mounts and the reflections of calcite and/or quartz used as calibrant. The clay fraction was analysed with oriented mounts [34] [146]. The air-dried and glycol-solvated XRPD traces were analysed with NEWMOD II software [162] to identify the phases involved and understand if interstratified clay minerals are present.

This section is divided in three sub-sections presenting separately the data obtained from the four reaction stacks. The data are presented using a comparative approach between the “Encrusted” and the “Soft” domains in order to highlight the different processes happening in the two layers.

In this chapter, only the key regions of interest in 2θ are depicted. Complete XRPD traces are available in appendix folder 5.3. This chapter concludes with a comparative analysis of the time-dependant behaviour of the four stacks and their constituent layers.
5.5.1 Stack 2 – Control Sample (12 months)

Stack 2 contained only the control vessel, consisting of bentonite alone reacted for one year. At the time of extraction the sample featured one encrusted layer at the interface with the sintered glass disc with a thickness between 2 and 3 mm, sometimes thicker (up to 5 mm) around the walls of the vessel (similar to Figure 5-16).

![Figure 5-12: Air-dried and glycol-solvated samples from the “soft” (A) and “encrusted” (B) areas of the control bentonite vessel of stack 2.](image)

The sample from the “soft” area (Figure 5-12A) follows the classic behaviour for a Na-montmorillonite, with a symmetric basal reflection with d₀₀₁ spacing 12.2 Å (7.3°2θ), that expands to 16.8 Å (5.1°2θ) upon glycol-solvation, giving a very narrow and symmetric peak. The glycol-solvated sample features the rational sequence of 0₀₁ reflections. Upon heating at 400°C the spacing collapses to 10 Å with no further collapse on heating at 550°C (Figure 5-13A).

The sample from the “encrusted” area (Figure 5-12B), features a considerably less intense basal reflection (centered at 7.2°2θ, equivalent to a d₀₀₁ spacing of 12.4 Å) with a well-developed left shoulder in the region around 6.5°2θ. A very low, broad and asymmetric basal reflection is usually indicative of the presence of a random mixture of clays or interstratified clay minerals [163] [164].

The glycol-solvated trace of the clay fraction of the encrusted layer does not show the characteristic rational sequence of 0₀₁ reflections (Figure 5-12B). The presence of a
clear reflection between 5.3°2θ and 8.7°2θ in the glycol-solvated trace is an indication of presence of ordered I/S [165]. However, considering the position at 13.4Å, this could also be attributed to the presence of dioctahedral vermiculite.

After heating at 400°C, the d001 spacing of the clay from the encrusted layer collapses to 12.2Å, coupled with a significant decrease of peak intensity (Figure 5-13B). After heating at 550°C the reflection is further decreased in intensity so that the peak is almost absent (Figure 5-13B). This behaviour may be indicative of a random mixture of smectite and vermiculite [146].

**Figure 5-13: 400°C and 550°C heated samples from the “soft” (A) and “encrusted” (B) areas of the control bentonite vessel of stack 2.**

XRPD of the accessory minerals of “encrusted” layer (Figure 5-14) shows how in both areas there has been a change in accessory phases. Feldspars and quartz decrease from the Soft to the encrusted sample. Muscovite and cristobalite peaks are no longer visible in the reacted samples but calcite peaks appear in both samples. The bulges visible in the regions 34-37°2θ, 47-49°2θ and around 56°2θ might be due to presence of CSH/C(A)SH phases with poor crystallinity. No peaks related to zeolites are visible.

XRPD analysis of the random mounts (Figure 5-15) show one main difference between the “encrusted” and “soft” areas: the presence of a sharp and very intense reflection at
11.3°2θ related to a very well crystallized AFm (hydrated calcium aluminate) phase called hydrocalumite (Ca₄Al₂O₆Cl₂ * 10H₂O).

Figure 5-14: XRPD traces of coarse accessory phases in the “encrusted” and “soft” areas of the control bentonite vessel.

Figure 5-15: XRPD traces of random mounts of samples from the “encrusted” and “soft areas of the control bentonite vessel.
5.5.2 Stack 3A – 4 months

The samples from stack 3A were extracted 4 months after the beginning of the experiment.

After the removal of the sinter glass disc and the extraction of the sample the matrix featured the presence of a light-coloured thin (2-3 mm thick) layer of encrusted material at the interface between sinter glass disc and matrix, and then a lower layer made of grey bentonite embedding the magnets (Figure 5-16).

![Figure 5-16: Post-extraction photograph of uncoated Nd-Fe-B + bentonite sample. The cylinder is 5 cm in diameter and 1 cm in height. The sample is shown upside-down but the thin “encrusted” layer is visible at the bottom. Two patches of orange-coloured precipitates are visible and may be caused by precipitation of Fe oxyhydroxides or, more likely, by precipitation of plastic corrosion-related phases.](image)

Figure 5-16: Post-extraction photograph of uncoated Nd-Fe-B + bentonite sample. The cylinder is 5 cm in diameter and 1 cm in height. The sample is shown upside-down but the thin “encrusted” layer is visible at the bottom. Two patches of orange-coloured precipitates are visible and may be caused by precipitation of Fe oxyhydroxides or, more likely, by precipitation of plastic corrosion-related phases.

![Figure 5-17: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.](image)

Figure 5-17: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.
Samples from the “soft” area have narrow and intense reflections with $d_{001}$ spacing of 12.4 Å with just a small left shoulder outlined (Figure 5-17A). The glycol-solvated traces (Figure 5-17B) feature the classic expansion of $d_{001}$ spacing to 17 Å for Na-montmorillonites; the shifts in the position of the main basal reflection registered for the samples closest to the water source (coated and uncoated Nd-Fe-B vessels) are most likely related to a smaller ethylene glycol-smectite complex thickness [165].

The samples from the “encrusted” layers feature low and noisy reflections with a pronounced left shoulder. The samples closer to the water source (coated and uncoated Nd-Fe-B vessels) show a flat left shoulder, which might be caused by presence of random mixtures of clay minerals. Glycol-solvated samples feature low reflections with a clear double peak. One is centered at 16.9 Å and one at 13.4 Å.

After heating at 400°C (Figure 5-19) all samples showed partial collapse of the clay $d_{001}$ spacing and also a considerable weakening of the reflection intensity. The samples from the “encrusted” area (Figure 5-19C) feature partial collapse of $d_{001}$ spacing to 12.5 Å and 12.1 Å for the coated and the uncoated Nd-Fe-B vessel samples.
Figure 5-19: 400°C- and 550°C-heated clay fraction of samples from the “encrusted” and “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference. The traces of the “encrusted” areas of SmCo and AlNiCo samples are not shown because the basal reflection had been destroyed upon heating.

Interestingly, the samples from the “soft” area (Figure 5-19A) feature partial collapse of d_{001} spacing to 12.1Å for the coated and uncoated Nd-Fe-B samples and 11.9Å for...
the SmCo and AlNiCo samples. A similar behaviour was registered also for the samples reacted with 0.1M NaOH solution in the batch experiment and in the equivalent control sample. In this case the partial collapse might be due to the presence of random interstratification (no peak is visible in the 5.3-8.7Å area of the glycol-solvated traces, so presence of ordered I/S interstratification is excluded), with a predominant smectitic component (>90%) [165].

After heating at 550°C (Figure 5-19B, D) all samples feature collapse of the d001 spacing to 10Å, with slight increase of peak intensity.

The comparison between the XRPD traces of accessory minerals in the “encrusted” areas (Figure 5-20) shows that the coarse material is predominantly composed by calcite, with minor quartz and feldspars.

No traces of cristobalite are visible. A strong decrease in the quantity of quartz and feldspars is detected, consistent with dissolution processes taking place, releasing silicon, potassium, magnesium and sodium into solution. The peak of muscovite at

![Figure 5-20: XRPD traces of coarse accessory phases in the “encrusted” areas. The intensity of MX80 profile was lowered 5 times for ease of display.](image-url)
9°20 is absent and peaks of newly formed phases appear, such as hydrocalumite (at 11.3°20 in the red trace). Peaks of CSH phases, such as tobermorite, are not visible possibly because of their poor crystallinity.

![Diagram of Accessory Minerals - "Soft areas"](image)

**Figure 5-21: XRPD traces of coarse accessory phases in the “soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display.**

The XRPD traces of the coarse accessory minerals in the “soft” areas (Figure 5-21) feature similar profiles to the MX80 starting material with the intensity of the peaks reduced. The vessel closer to the water reservoirs feature overall lower intensity peaks of the initial accessory minerals, and slightly higher calcite peaks.

The analysis of XRPD traces of accessory minerals shows the disappearance of most of the original phases in the “encrusted” areas and a diminishing intensity of the peaks in the “soft areas”. This is considered to be caused by dissolution (or partial dissolution) of feldspars and quartz and cristobalite in alkaline solutions. The elements released into solution for the dissolution of these phases are believed to have played a crucial role in the dissolution/reprecipitation processes affecting the montmorillonite in the “encrusted” areas and secondarily in the “Soft” areas.
It is unknown which steps occurred to form the I/S interstratifications, but a dissolution/reprecipitation process [53] coupled with a transformation from a K-smectite layer to illite layer reaction [166] would be consistent with previous experimental observations.

The analysis of the random mounts allowed further constraints on the presence of cement porewater-related materials. As visible from Figure 5-22, a clear peak centered at ca. 11.3°2θ for the coated Nd-Fe-B sample is present and another at around 10.8°2θ appears in the uncoated Nd-Fe-B sample.

Both peaks are related to AFm-related phases, and are identified as belonging to minerals of the hydrocalumite family, also known as Friedel’s salt [167]. This phase is stable at room temperature and mainly occurs as an alteration product of cement paste in saline environments [168]. The relative displacement of the peaks is likely due to reflect slightly different compositions of the two phases; the peak at 10.8°2θ is found consistent with a monoclinic AFm related phase with formula Ca₂AlCl(OH)₆(H₂O)₂ [169], whereas the peak at 11.3°2θ with a phase isostructural with a rhombohedral Ca₄Al₂O₆Cl₂·10H₂O compound [170].

Figure 5-22: XRPD traces of random mounts of samples from the “encrusted” areas.
The bulges visible in the 48.5-56.0°2θ range are related to the presence of poorly crystallized CSH (tobermorite-clinotobermorite) and zeolites (Ca-rich phases of the heulandite-clinoptilolite series).

![Random Mounts - "Soft areas"](image)

**Figure 5-23: XRPD traces of random mounts of samples from the “soft” areas.**

The random mounts of the “soft” areas (Figure 5-23) feature the typical patterns for a montmorillonite, with the exception of the halite peaks and the bulge in the range 52-56°2θ, probably again related to the presence of poorly crystallized CSH phases and zeolites.

5.5.3 **Stack 3B – 8 months**

The vessels contained in Stack 3B were extracted after 8 months, with the exception of the SmCo vessel, which suffered a failure of the sealing system (See Section 3.3.1) and had to be aborted after 5 months. Hence, the XRPD analysis of the SmCo vessel matrix is not presented in this section; it is available in the appendices Folder 5.4.
At the time of extraction all the uncoated magnetic samples featured heavy traces of corrosion, with the uncoated Nd-Fe-B magnets presenting, at the interfaces with the bentonite matrix, small amounts of a green-coloured flaky material (Figure 5-24A). Fe (oxy)hydroxides precipitated at the interface between all the magnetic materials and the matrix and no change in the matrix colour was detected for the samples apart from those in the uncoated Nd-Fe-B/bentonite vessel. All vessels presented an encrusted layer at the interface with the filtering system (Figure 5-24B) with a thickness between 2 and 3 mm.

Figure 5-25: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.
Air-dried and glycol-solvated XRPD traces of the “soft” clays (Figure 5-25) show the typical Na-montmorillonite behaviour, with the rational series of 00l reflections in the glycol-solvated traces. The glycol-solvated traces (Figure 5-25B), however, also present a weak and broad reflection at 11.45Å. According to Srodón [165] the presence of a peak in the 5.3-8.7°2θ area of the glycol-solvated indicates the presence of some kind of ordered I/S interstratification. Upon heating at 400°C, the samples from the “soft” areas feature collapse of the d001 spacing to10Å; however, the AlNiCo and uncoated Nd-Fe-B samples show a pronounced reflection centered around 11.47Å (Figure 5-27A). After heating at 550°C all traces feature only one distinctive reflection at 10Å (Figure 5-27B). The samples from the “soft” areas show the classic behaviour of smectitic clay. However, the presence of a reflection at 7.5°2θ in the air-dried traces and the behaviour upon heating to 400°C suggest the presence of small quantities of ordered interstratified I/S within predominantly pure Na-montmorillonite.

The air-dried samples from the “encrusted” areas (Figure 5-26A) show very low and broad basal reflections, with pronounced shoulders on the lower 20 side of the peak, in the area 5.6-6.1°2θ. After glycol-solvation (Figure 5-26B), the basal reflection migrates towards lower diffraction angles, corresponding to a d001 spacing of 16.8Å, but a reflection at 13.5Å appears for the AlNiCo and uncoated Nd-Fe-B samples and
another at 11.43Å for the coated Nd-Fe-B sample. The presence of a clear second peak in the 5.6-8.7°2θ area together with the absence of the rational sequence of 00l reflections indicates the presence of ordered interstratifications

Figure 5-27: 400°C- and 550°C-heated clay fraction of samples from the "encrusted" and "soft" areas of bentonite matrix. The peaks relative d-spacing are shown as reference.
The samples from the “encrusted” areas exhibit complex basal reflections after heating at 400°C (Figure 5-27C). The coated Nd-Fe-B sample features two clear reflections at 11.86 and 10Å, whereas the uncoated Nd-Fe-B sample only one reflection, very broad and low at 11.86Å. The AlNiCo sample exhibits a low and broad reflection at 12.23Å. Upon heating at 550°C, these reflections are destroyed or further decreased in intensity (Figure 5-27D).

The samples from the “encrusted” areas therefore are observed to exhibit complex basal reflections even at high temperatures. Random mixtures of interstratified clay minerals such as illite/montmorillonite and dioctahedral vermiculite/montmorillonite might produce these reflections.

![Accessory Minerals - "Encrusted areas"](image)

*Figure 5-28: XRPD traces of coarse accessory phases in the “encrusted” areas. The intensity of MX80 profile was lowered 5 times for ease of display.*

XRPD analysis on the accessory phases of the “soft” (Figure 5-29) and “encrusted” (Figure 5-28) areas show clearly how in both areas there are major decreases in the intensities of feldspars and quartz, and a complete disappearance of the reflections of muscovite and cristobalite in the “encrusted” areas. The muscovite basal reflection
disappears only in the trace of the “soft” sample closest to the water source (coated Nd-Fe-B vessel). The bulges the regions at 33-36°20, 48-52°20 and the pronounced shoulders on the main calcite reflection (29°20) are related to the presence of poorly-crystalline hydrated calcium silicates (CSH) phases. In Figure 5-28, it is visible how the distance from the reservoir influences the dissolution of the accessory minerals in the “encrusted” areas, with the peaks of the feldspars being absent in the coated Nd-Fe-B sample, closest to the water reservoir.

![Accessory Minerals - "Soft areas"

Figure 5-29: XRPD traces of coarse accessory phases in the “soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display.

The analysis of the random mounts (Figure 5-30 and Figure 5-31) confirms the presence of halite (NaCl) in all the samples and an intense peak located at 21.6°20 in the “soft” area of the coated Nd-Fe-B sample (Figure 5-31). This peak, also found in the equivalent sample of Stack 3A, is attributed to cristobalite. The origin of this peak is unknown.
Figure 5-30: XRPD traces of random mounts of samples from the “encrusted” areas.

Figure 5-31: XRPD traces of random mounts of samples from the “soft” areas.
5.5.4 *Stack 1 – 12 months*

The vessels of this stack underwent reaction for one year. At the time of extraction, all four samples featured an encrusted area 2-4 mm thick, usually thicker around the vessel walls. This “encrusted” area appeared white in colour and flat. No crystals were visible. In the areas close to the walls of the vessels, the material appeared layered with thin white layers sandwiching grey-coloured layers (Figure 5-32).

![Figure 5-32: Close-up photograph of the “encrusted” clay material sampled in the coated Nd-Fe-B vessel. In the red circle, the layered material is visible.](image)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-dried - &quot;Soft clays&quot;</td>
<td>Glycol-solvated - &quot;Soft clays&quot;</td>
</tr>
<tr>
<td>12.4Å</td>
<td>16.9Å</td>
</tr>
</tbody>
</table>

![Figure 5-33: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “soft” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.](image)
Figure 5-34: XRPD traces of air-dried (A) and glycol-solvated (B) clay fraction of samples from the “encrusted” areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

The XRPD traces of the samples from the “soft” areas show the classic behaviour of Na-montmorillonite, with an increasing d₀₀₁ spacing from 12.4Å to 16.9Å (Figure 5-33A/B) upon glycol-solvation and presence of the rational sequence of 00l reflections in the glycol-solvated traces (Figure 5-33B).

Upon heating at 400°C three samples from the “soft” areas show collapse of d₀₀₁ spacing to 12Å, with a pronounced right shoulder for the SmCo sample; the coated Nd-Fe-B sample features a very low and broad reflection, centered at approximately 10Å (Figure 5-35A). After 550°C-heating all reflections feature comparable intensities and correspond to d₀₀₁ spacing of 10Å (Figure 5-35B).

The samples from the “encrusted” areas show very low and broad basal reflections, with a d₀₀₁ spacing around 12.4Å (Figure 5-34A) and pronounced shoulders on the lower 2θ side of the peak. The glycol-solvated traces (Figure 5-34B) show migration of the main basal reflection towards lower diffraction angles, corresponding to a d₀₀₁ spacing of 16.8Å, but a reflection, or a broad flat shoulder, appears at 13.5Å in all four samples.

As seen for the samples from the “encrusted” areas in stack 1, 3A and 3B, the presence of a clear second peak in the 5.6-8.7°2θ area together with the absence of the rational sequence of 00l indicates the presence of ordered interstratifications.
Figure 5-35: 400°C- and 550°C-heated clay fraction of samples from the "encrusted" and "soft" areas of bentonite matrix. The peaks relative d-spacing are shown as reference.

The samples from the “encrusted” areas show a 001 reflection destroyed already after heating at 400°C for the coated and uncoated Nd-Fe-B samples; the other two samples feature very weak and broad humps centered approximately around 11.6 and 12.1Å (Figure 5-35C). After heating at 550°C, the basal reflection is destroyed in all four samples (Figure 5-35D).
The analysis of the accessory minerals revealed a constant amount of calcite forming for all samples from the “encrusted” areas, and the presence of CSH phases forming the right shoulder of the main calcite reflection at 29°2θ (Figure 5-36). The reflections for feldspars and quartz were reduced (for the samples away from the reservoir) or disappeared (for the samples close to the reservoir); the muscovite reflection also disappeared.

The XRPD traces of accessory minerals from the “soft” areas featured all the reflections of feldspars and quartz, although reduced in intensity (Figure 5-37). Some intense reflections in the area 35-52°2θ have been identified as calcium silicate hydrides (CaH₄Si₂O₇), brucite (MgOOH) and boehmite (AlOOH).
Figure 5-37: XRPD traces of coarse accessory phases in the “Soft” areas. The intensity of MX80 profile was lowered 5 times for ease of display. The asterisk marks 2M1 muscovite or Illite.

The XRPD traces for the accessory phases in the “soft” areas are shown in Figure 5-37. A sharp reflection is visible at 9°2θ (in the uncoated Nd-Fe-B and SmCo samples), corresponding to the muscovite reflection in the original material. Considering the differences in intensity with the same reflection on the samples from the other stacks (Figure 5-14, Figure 5-21 and Figure 5-29) it is possible that this sharp reflection also marks the presence of newly crystallized 2M1 illite.
Figure 5-38: XRPD traces of random mounts of samples from the “encrusted” areas. The asterisk marks a sharp reflection belonging to calcium aluminium oxide phase.

Figure 5-39: XRPD traces of random mounts of samples from the “soft” areas.
The random mounts of the “soft” area samples are similar to the samples seen in the previous stacks (Figure 5-39). The XRPD traces of the random mounts of the “encrusted” area samples (Figure 5-38) show the reflection of hydrocalumite at 11.3°2θ and a sharp reflection at 18°2θ; the latter has been identified as the main reflection of a mineral belonging to the calcium aluminate group. The identification of the precise species is difficult as only this reflection is available but the mineral can be constrained to belong to the mayenite (dodecacalcium hepta-aluminate) supergroup [171]. Precipitation of such phases suggests local environments characterised by high calcium and aluminium concentrations.

5.5.5 Summary of clay behaviour

The matrix samples from the vessels of the confined-fluid flow experiments feature very interesting characteristics. All show a 2-4 mm thick encrusted area in contact with the filtering system, characterised by the presence of an almost constant amount of calcite in every sample and the presence of phases characteristic of weathered or hydrated cements like hydrocalumite (Ca$_2$AlCl(OH)$_6$(H$_2$O)$_2$), a mayenite-like phase (Ca$_{12}$Al$_{14}$O$_{33}$), CSH or C(A)SH phases. Amorphous silica is present in all encrusted layers. The “soft” areas underneath the encrusted areas feature characteristics of the accessory phases similar to the initial unreacted MX80 bentonite.

Mineralogical changes to the clay occur in both the “encrusted” or “soft” areas. The clay fraction from the “encrusted” areas in all samples feature very low and broad basal reflections centered at 12.4Å with a broad shoulder at lower diffraction angles. After glycol-solvation, all traces feature a low and broad double peak in the 3-10°2θ area and do not show the rational sequence of basal reflections. The first peak is centered at 16.8Å, whereas the second at 13.4Å; only one sample features a second peak at 11.43Å. The presence of a double peak in the EG traces in the 5.6-8.7°2θ area is usually indicative of the presence of interstratified clays [165]; the registered peak broadening may be caused by presence of random mixtures of several clays with very close peak positions. The peak at 13.4Å is indicative of the presence of a non-swelling clay phase that could be either dioctahedral vermiculite or dioctahedral chlorite. However, given the composition of the initial material and the assumption that the diffusing hyperalkaline solution is Ca-saturated and very low in Mg, the second phase
is most likely to be dioctahedral vermiculite. The presence of a broad peak at 11Å after 400°C-heating suggests that the mineral belongs to the vermiculite family.

The samples from the “soft” domains show substantially unchanged air-dried and glycol-solvated traces compared to the starting MX80 material in most of the samples. However, presence of random or ordered I/S is detected clearly in the samples of stack 3B with the glycol-solvated trace showing a double peak at 11.43Å but cannot be excluded in all the other samples, considering that most of the samples feature an anomalous partial collapse to only 12Å after heating at 400°C.

5.6 Confined Fluid Flow Experiments – Concluding remarks

The time-dependent experiments under conditions similar to those expected in a “time-evolved” repository, involving saturation of the bentonite buffer with hyperalkaline solutions derived from cement leaching, leads to very interesting results.

The chemical conditions here explored are not significantly altered from those expected in an underground facility; the main difference is that in this study deionised water mixed with 0.273M of NaCl has been used to react with the NRVB cement instead of the Allard reference groundwater used in other studies.

The main difference between a real underground setting and the experimental design is that in this project powderized bentonite was used instead of compressed bentonite. This difference it is believed to play a marginal role in the corrosion of the magnets, given that is more the composition of the solution and the presence or absence of the bentonite matrix that are reckoned to contribute to the variations of the intrinsic magnetic field of the magnets.

Under the conditions explored here, the results allow the list of potential candidate magnetic materials to be narrowed down to two: Nd-Fe-B permanent magnets and SmCo permanent magnets.

The Nd-Fe-B permanent magnets confirmed the behavioural trend already observed in the batch experiments, with a very sharp transition of the uncoated magnets from single-domain behaviour to superparamagnetic behaviour. These magnets potentially start losing their hysteretic properties immediately during water saturation of the bentonite buffer.
Coated Nd-Fe-B magnets also exhibited very clear changes in their hysteretic and thermomagnetic behaviour, with a significant decrease of the coercive field between 8 and 12 months and remanence reduced by 50% from the starting material. This suggests that coated Nd-Fe-B magnets, after some delay due to the presence of the coating, behave similarly to the uncoated ones.

The SmCo magnets, despite not exhibiting great changes in their hysteretic properties, featured changes in the amount of the preserved main magnetic phase and the formation of soft magnetic phases in the thermomagnetic analysis.

AlNiCo magnets were corroded but the corrosion did not lead to significant alteration of either their hysteretic or thermomagnetic properties. These samples were likely only superficially oxidised, and the oxidation did not damage the underlying magnetic domains.

Observations on the variation of the saturation magnetization of the Nd-Fe-B samples indicated that the decreasing amounts of hard magnetic phases is not always balanced by the formation of other hard or soft magnetic phases. The consequent reduction of the magnetization saturation of the samples essentially reflects the precipitation of neo-formed, corrosion-related, non-ferromagnetic materials (Nd hydrides or hydroxides, Fe oxides or (oxy)hydroxides).

More importantly, the corrosion of the permanent magnets did not lead to the formation of non-swelling clays. All the changes that occurred to the clay matrix, such as formation of an encrusted area with complex mixtures of sheet silicates (vermiculite and montmorillonite) and formation of ordered or random I/S in the soft matrix are found to be not related to the magnet corrosion process, but to the interaction between the diffusing hyperalkaline fluids and the bentonite matrix.

The transformations occurring to the bentonite matrix are interpreted related to a dissolution/reprecipitation process involving either the clay fraction or the accessory minerals. At the interface, the reactions lead to the formation of an Encrusted layer, which might have acted as a chemical buffer that reduced the pH of the solution diffusing in the underlying soft layer, so preventing further deeper alteration of its mineralogy.
The neo-formed, corrosion related phases were all located in the immediate vicinity of the magnets, but was not possible to identify them through X-ray diffraction because they were amorphous or not nanoparticulate over the duration of these experiments. It was possible to identify many accessory phases related to the bentonite/hyperalkaline fluid interaction (hydrocalumite, CSH, etc.), but the newly formed phases were certainly dominated by calcite, which was ubiquitously present in all samples in almost constant amounts.
Table 5.1: Composition and magnetic properties of magnets and relative encasing matrix extracted from Stack 3A. Within square brackets, the values of the magnetic properties of the raw materials are presented for comparison.

### Magnets

<table>
<thead>
<tr>
<th>Coating</th>
<th>Degree of corrosion</th>
<th>Corrosion-related phases</th>
<th>Remanence</th>
<th>Saturation magnetization</th>
<th>Coercivity</th>
<th>Curie Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated NdFeB</td>
<td>Low</td>
<td>NdFeB hydrides</td>
<td>84 (A* m²)/kg [145.3]</td>
<td>131.05 (A* m²)/kg [152.83]</td>
<td>1.2T [1.2]</td>
<td>310°C [310] Second Curie point at 330°C</td>
</tr>
<tr>
<td>Uncoated NdFeB</td>
<td>High</td>
<td>NdFeB hydrides, Nd hydrides, Fe-oxides/(oxy)hydroxides</td>
<td>12.9 (A* m²)/kg [145.3]</td>
<td>97.9 (A* m²)/kg [152.83]</td>
<td>0.1 T [1.2]</td>
<td>Analysis failed for explosion of sample holder</td>
</tr>
<tr>
<td>SmCo</td>
<td>Low</td>
<td>Near equiatomic Fe-Co phase</td>
<td>99 (A* m²)/kg [99]</td>
<td>102.3 (A* m²)/kg [102.3]</td>
<td>2.5 T [2.5]</td>
<td>825°C [825] Second Curie point at 960°C</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>Very low</td>
<td>none</td>
<td>40.8 (A* m²)/kg [44.8]</td>
<td>153.76 (A* m²)/kg [163]</td>
<td>0.065T [0.065]</td>
<td>860°C [860]</td>
</tr>
</tbody>
</table>

### Clay matrix

<table>
<thead>
<tr>
<th>Coating</th>
<th>&quot;Encrusted&quot; area Clay fraction</th>
<th>&quot;Encrusted&quot; area Coarse fraction</th>
<th>&quot;Soft&quot; area Clay fraction</th>
<th>&quot;Soft&quot; area Coarse fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated NdFeB</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Hydrocalumite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Minor ordered LS</td>
<td>Calcite, Quartz, Sanidine, Albite</td>
</tr>
<tr>
<td>Uncoated NdFeB</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Hydrocalumite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Minor ordered LS</td>
<td>Calcite, Quartz, Sanidine, Albite</td>
</tr>
<tr>
<td>SmCo</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Minor ordered LS</td>
<td>Calcite, Quartz, Sanidine, Albite</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Minor ordered LS</td>
<td>Calcite, Quartz, Sanidine, Albite</td>
</tr>
</tbody>
</table>
### Stack 3B – 8 months

#### Magnets

<table>
<thead>
<tr>
<th></th>
<th>Degree of corrosion</th>
<th>Corrosion-related phases</th>
<th>Remanence</th>
<th>Saturation magnetization</th>
<th>Coercivity</th>
<th>Curie Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated NdFeB</td>
<td>Low</td>
<td>NdFeB hydrides</td>
<td>117.5 (A·m²/kg [145.3]</td>
<td>149.57 (A·m²/kg [152.83])</td>
<td>1.2T [1.2]</td>
<td>310°C [310]</td>
</tr>
<tr>
<td>Uncoated NdFeB</td>
<td>High</td>
<td>NdFeB hydrides, Nd hydrides, Fe-oxides (oxy)hydroxides</td>
<td>0 (A·m²/kg [145.3])</td>
<td>96.95 (A·m²/kg [152.83])</td>
<td>0 T [1.2]</td>
<td>380°C [310]</td>
</tr>
<tr>
<td>SmCo (*)</td>
<td>Low</td>
<td>Near equiaxonic Fe-Co phase</td>
<td>99 (A·m²/kg [99])</td>
<td>102.3 (A·m²/kg [102.3])</td>
<td>2.45 T [2.5]</td>
<td>$225^\circ$C [225]</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>Very low</td>
<td>None</td>
<td>42.7 (A·m²/kg [44.8])</td>
<td>159.86 (A·m²/kg [163])</td>
<td>0.065 T [0.065]</td>
<td>$860^\circ$C [860]</td>
</tr>
</tbody>
</table>

#### Clay matrix

<table>
<thead>
<tr>
<th></th>
<th>“Encrusted” area Clay fraction</th>
<th>“Encrusted” area Coarse fraction</th>
<th>“Soft” area Clay fraction</th>
<th>“Soft” area Coarse fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated NdFeB</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Subordinated ordered I/S</td>
<td>Calcite, Quartz, Sanidine, Albite, Muscovite, Cristobalite</td>
</tr>
<tr>
<td>Uncoated NdFeB</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Subordinated ordered I/S</td>
<td>Calcite, Quartz, Sanidine, Albite, Muscovite</td>
</tr>
<tr>
<td>SmCo (*)</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Subordinated ordered I/S</td>
<td>Calcite, Quartz, Sanidine, Albite, Muscovite</td>
</tr>
<tr>
<td>AlNiCo</td>
<td>Interstratified Al-vermiculite/Na-montmorillonite</td>
<td>Calcite, Quartz, Albite, Halite</td>
<td>Na-montmorillonite Subordinated ordered I/S</td>
<td>Calcite, Quartz, Sanidine, Albite, Muscovite</td>
</tr>
</tbody>
</table>
Stack 1 – 12 months

**Magnets**

| Coated NdFeB | Low | NdFeB hydrides | 65.8 (A·m²·kg) | 13.46 (A·m²·kg) | 0.61 T | 350°C [310] |
| Coated NdFeB | High | NdFeB hydrides, Nd hydrides, Fe-oxides/oxyhydroxides | 0 (A·m²·kg) | 121.39 (A·m²·kg) | 0 T [1.2] | Sample exhibited negative signal values—loss of thermomagnetic properties |
| SmCo | Low | Near equiatomic Fe-Co phase | 99 (A·m²·kg) | 102.3 (A·m²·kg) | 2.3 T [2.5] | $25^\circ$C [25°C] Second Curve point at 960°C |
| AlNiCo | Very low | none | 43.7 (A·m²·kg) | 157.34 (A·m²·kg) | 0.065 T [0.065] | $80^\circ$C [560°C] |

**Clay matrix**

| Coated NdFeB | Interstratified Al-vermiculite/Na-montmorillonite | Calcite, Quartz, Albite, CSH phases, Hydrocalumite | Na-montmorillonite | Calcite, Quartz, Sphalerite, Albite, Muscovite, Iliite, CSH, Boehmite |
| Coated NdFeB | Interstratified Al-vermiculite/Na-montmorillonite | Calcite, Quartz, Albite, CSH phases | Na-montmorillonite | Calcite, Quartz, Sphalerite, Albite, Muscovite, Iliite |
| SmCo | Interstratified Al-vermiculite/Na-montmorillonite | Calcite, Quartz, Albite, CSH phases | Na-montmorillonite | Calcite, Quartz, Sphalerite, Albite, Muscovite, Iliite |
| AlNiCo | Interstratified Al-vermiculite/Na-montmorillonite | Calcite, Quartz, Albite, CSH phases | Na-montmorillonite | Calcite, Quartz, Sphalerite, Albite, Muscovite, Brucite |
6 Conclusions
Remote monitoring of the Engineered Barrier Systems in a Geological Disposal Facility for High Level Waste is a huge technical challenge that attempts to combine the necessity of monitoring the safety and stability of the barrier with the need of preserving the barrier itself from a possible monitoring-induced damage.

This thesis has offered a novel and innovative concept for the remote monitoring of the stability of the Engineered Barrier, using mineral magnetism.

The idea behind the concept is that the corrosion-induced changes in the magnetic field of selected permanent magnets could be useful to detect water saturation and/or water chemistry variations in the clay buffer area without putting at risk the stability of the buffer itself.

This project has considered a two-stage approach proceeded by a robust literature study. In the first experimental stage (the “batch” experiments), different magnetic materials (both synthetic and natural) were reacted in a simple fashion within or not bentonite matrix to test their reactivity under “extreme” conditions. That experimental stage allowed the list to be narrowed down to three potential candidates.

These three magnets were then tested in the second experimental stage, where the mixture of magnets and bentonite was reacted under confined-fluid flow and constant chemical conditions, to simulate the environmental settings of an underground repository.

This thesis has demonstrated that the use of mineral magnetism is a very useful tool to monitor clay saturation and/or water chemistry variation through time identifying two permanent magnets that showed excellent reactions: Nd-Fe-B and SmCo magnets.

The comparison of the data collected after the batch and the confined fluid flow experiment allows to state that Nd-Fe-B magnets have the highest chemical reactivity under all the environmental conditions explored. The loss of magnetic properties is extremely fast if compared to the other candidates (the uncoated Nd-Fe-B magnets exhibited complete loss of hysteretic properties even after 4 months), so it is possible to assert that these magnets have a great potential to be used as sensors for clay buffer water saturation.
SmCo magnets showed less dramatic changes in hysteretic properties in the confined fluid flow experiments, but quite striking variations in coercivity and remanence in the batch experiments especially when reacted with saline solutions. Hence, these magnets are potentially considered good candidates for monitoring water chemistry variations through time.

The thesis has also demonstrated that the corrosion of the magnets does not cause any mineralogical perturbation to the clay barrier, not causing the formation of non-swelling clay phases at the clay/magnet interface.

Beside the demonstration of the feasibility of the concept, this project is intended as a starting point for further researches (see next chapter) but also wants to offer a simple description about the logistics and timescale of the monitoring. In the development of a remote, self-generating and passive monitoring system, a timescale of minimum 100 years is required in order to guarantee the safety of the underground operators, but an extensive lifespan is preferable to monitor the repository post-closure. Considering a vertical depositional borehole with a bentonite sleeve with axially magnetised permanent magnet discs embedded in a particular geometry (Figure 7-1), the overall magnetic field and its corrosion-driven changes can easily be measured by magnetometers situated on top of the borehole-sealing plug or on galleries dozens of meters above the service galleries.

7 Future developments

The next step in this promising research field is the implementation of the knowledge of the corrosion mechanisms, through focused corrosion experiments in a broad range of possible environmental conditions, to potentially develop a model for the temporal evolution of the magnetic properties of the two selected candidates.

The future project will be divided in three principal phases.

The first phase will be focused on the development, realization and optimization of an engineered magnetic system and the construction of a newly designed reaction cell where the magnetic system will be tested.

Based on preliminary calculations (Harley et al., submitted), a single N45 Nd-Fe-B disc with radius of 20 mm and thickness 5 mm produces an axial flux density,
immediately above the magnet, of 10 nT at a distance of 5.12 metres immediately above the magnet, increasing to 100 nT at 2.38 metres and 1000 nT at 1.1 metres. These flux densities above a single magnet decrease significantly laterally over only millimetres, but the intention of phase 1 of this research is to minimize the lateral gradient and produce a broad, flat-topped, initial magnetic anomaly over the target EBS through careful design and optimization of the magnetic system geometry (disc size, magnet spacing, 2d and 3d configurations of the magnet array).

This magnetic system is made of an array of magnets embedded in a bentonite sleeve (Figure 1) that, in the EBS concept, will surround the waste canisters. The design of the magnetic array is essential to ensure the maximization of the signal output either in a laboratory-based experiment or ground-based experiments. In order to achieve this first target, an easy-to-assemble and cheap mock-up cell made of non-magnetic material will be developed. This cell will be made by stackable plastic discs (with a thickness between 5 and 10 cm) in which several cylindrical holes are drilled to host the magnets.

The magnets will then be inserted in the holes in different geometries, and the discs stacked. The magnetic field will then be measured to find which array geometry optimises best the overall magnetic field in output and reduces the lateral interferences between the single fields. These measurements will be compared with the predictions of desk-based simulations and finite element modelling applied to conceptual magnetic array configurations.

The second phase of this project will be focused on the development of a new type of imposed fluid-flow reaction cell that constitutes a refinement of cells developed by previous researchers. The key objective is to develop an innovative, reusable and cost-effective reaction cell that can withstand elevated swelling pressures generated by the saturated clay sleeve and which is not affected by the highly aggressive fluids that are considered to diffuse within the clay.
The cell will be based on a design similar to the transport cells developed by Fernandez et al., (2006) and reaction cells developed by Fernandez et al., (2009). The reaction cell to be developed here will be manufactured out of a block of rock (ideally granite) and will have an internal diameter of 20-40 cm and an external diameter of maximum 80 cm. In contrast to the previous types of cell, which have applied an external heat source (e.g. an oven), in the proposed experiments the heat source will be internal (a plastic cylinder with an electric resistance capable of generating temperatures between 50 and 100°C). An internal heat source is essential in this type of experiment because it can be used to replicate a temperature gradient across the bentonite sleeve that is similar to the one expected in a repository as a consequence of heating from the radioactive waste canister. The fluid-flow (either saline or hyperalkaline solutions) will be imposed by a peristaltic pump connecting reservoirs isolated from atmospheric conditions to the base of the cell. The recirculation of solution is necessary to maintain...
a continuous supply of reactants and keep boundary conditions constant over the timespan of the experiment, simulating gradual saturation of the engineered barrier.

This research will focus on the real-time passive detection, via the multi-magnet system designed and optimised in the first phase of the research, of the saturation of the bentonite-based barrier in the presence of these hyperalkaline fluids and on the interactions occurring between bentonite and lower-pH fluids at temperatures between 70 and 100°C.

This research will employ materials that have previously been used, characterised and analysed in this PhD project. Those results will provide a reference database for comparisons to be made between real-time responses and magnet corrosion progress, and so contribute to and provide a foundation for this very distinct research trajectory. In this work the magnets will be tested as an array, a designed and optimised system, and the magnetic field variations arising in this system recorded in real time. This will, uniquely, enable critical monitoring parameters such as response time to solution ingress, bentonite saturation state and the impact of fluid chemistry to be determined.

Real-time magnetic fields will be recorded with modern ground-based magnetometers or a 3-axis fluxgate magnetometer. As modern ground-based and remote magnetometers can routinely measure with precisions of 0.1-1.0 nT (0.1-1 gamma), anomalies of the order of 10 nT are easily recorded and are assumed to provide a conservative lower limit of resolution for the method.

Individual laboratory experiments will be terminated when the registered magnetic field has reached the lower sensitivity limits of the magnetometers or, after pilot tests, when the characteristic response times are established. The experimental materials (magnets and bentonite clays) will be characterized following cessation of the experiment using the same instruments and approaches developed during this PhD, and the data compared. For example, the pristine and corroded magnets will be characterized using high-field SQUID immersion magnetometers and magnetometers with high-T control for Curie point analysis. Eventual characterization of antiferromagnetic or canted antiferromagnetic corrosion-related precipitates will be done using low-temperature magnetic susceptibility measurements. In order to evaluate the application of the approach from an engineering perspective the newly
designed reaction cell will be inspected and a report on its stability and performance will be issued after every experiment.

The third phase of the project will be directed at upscaling of the real-time experiments to deposition site scale within a GDF, and the testing of the magnetic arrays and response signals under those conditions. This field application and testing of the project is the most ambitious part of the project; it will require access to a rock laboratory outside the UK (Aspö in Sweden; Mount Terry in Switzerland) and the setting up of an of a scaled-up magnetic array that will be buried along with a heated canister, its overpack and bentonite-based EBS in a deposition borehole. This test site will be instrumented with magnetometers, and complementary environmental sensing systems (T, humidity, stress), and the progress of EBS saturation monitored using the novel magnetic monitoring system design developed and tested at smaller scale in phases 1 and 2 of the project.
8 Publications and conference posters
From this thesis work, the following papers have been published or are under review:


The following abstracts have been submitted to international conferences:


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