



Research Paper

Monitoring long-term evolution of engineered barrier systems using magnets: Magnetic response

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H I G H L I G H T S

- Nd-Fe-B magnets show time-dependent transition from ferromagnetic square-like to superparamagnetic loops upon corrosion.
- The changes in the hysteretic and thermomagnetic behaviour of Nd-Fe-B are related to the formation of hydride phases.
- SmCo magnets feature changes of the coercive field but not of the intrinsic hysteretic properties due to hydrides formation.
- AlNiCo magnets feature negligible deviations in remanence and saturation magnetization.

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Remote and non-destructive monitoring of the stability and performance of Engineered Barrier Systems for Geological Disposal Facility is gaining considerable importance in establishing the safety cases for Higher Activity Wastes disposal. This study offers an innovative use of mineral magnetism for monitoring groundwater saturation of the barrier. Four mixtures of permanent magnets (Nd-Fe-B, coated and uncoated; SmCo and AlNiCo) and bentonite were reacted for 4, 8 and 12 months with mildly-saline, high-pH leachates, representing the fluids saturating a time-evolved engineered barrier. Coupled hysteresis and thermomagnetic analyses demonstrate how Nd-Fe-B feature a time-dependent transition from square-like ferromagnetic to superparamagnetic loop via pot-bellied and wasp-waist loops, whereas SmCo and AlNiCo do not show so extensive corrosion-related variations of the intrinsic and extrinsic magnetic properties. This study allowed to identify magnetic materials suitable for shorter- (Nd-Fe-B) and longer-term (SmCo and AlNiCo) monitoring purposes.

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1. Introduction

One of the essential features of Geological Disposal Facility (GDF) concepts for the disposal of high-level radioactive waste in the deep sub-surface is the protection of radioactive waste canisters from corrosion in order to avoid or at least minimise the release of radionuclides into the near-field environment and beyond. To achieve this most Waste Management Organisations (WMOs) have developed safety cases based on the cumulative properties of multi-barrier systems composed by the waste canister, a bentonite sleeve around the canister with a thickness around 1 m and finally the geosphere itself.

The performance of the clay-based backfill material is a crucial factor to establish the safety case for the deep underground nuclear waste disposal; the backfill material should maintain its peculiar physico-chemical-mechanical characteristics, like very low porosity and hydraulic conductivity, through time.

However, the bentonite buffer will undergo mineralogical transformations that will affect its physio-chemical-mechanical properties because of interaction with hyperalkaline leachates coming from cementiferous backfill, Fe enrichment in the vicinities of the canister or ingress of groundwaters rich in potassium.

Monitoring of the GDF and its constituent parts is recognised internationally as being critical to decision-making during phased or staged disposal of radioactive waste [1,2]. Monitoring, via continuous or periodic observation and measurement, of the key thermal, mechanical, chemical and hydrological parameters of a GDF is not only required in order to evaluate the behaviour of the repository system and performance of the barriers in relation to their

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safety functions, but also to build and sustain public confidence in geological disposal [1–4].

Whilst the need for pre-construction and operational monitoring of a GDF is fully accepted by all WMOs and national programmes in accord with the requirements of the IAEA [3,5], the need for post-closure monitoring has until recently been questioned. One reason for this is that closure of a GDF would only occur once it is deemed, on the basis of all the pre- and operational monitoring coupled with forward modelling, to meet the standards required for post-closure safety.

As discussed in a previously published paper by Harley et al. most of the tested monitoring techniques require a power source to operate and their ability to monitor the useful parameters for the Engineered Barrier System (EBS) evolution is limited.

Hence, Harley et al. developed an alternative approach to in-situ monitoring of any bentonite-based EBS using magnetic materials; the concept underpinned in that study was on utilizing fluid-induced changes in the intrinsic magnetic properties of natural and synthetic materials to monitor the migration and recharge of fluids into the EBS of a bentonite-buffered GDF for high level waste.

This work represents a further refinement of the experiment described by Harley et al. [6], with the magnets/bentonite samples reacted in an environment considered being closer to the conditions of a time-evolved EBS. This paper investigates the effects of the corrosion process on the magnetic properties of the embedded magnets only; the evolution of the bentonite matrix will be investigated in another publication.

2. Literature review

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.

2.1. Nd-Fe-B permanent magnets

Research on corrosion studies of Nd-Fe-B 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 [7–11]. However, less work has been done on the corrosion in wet environments and in saturated and unsaturated soils.

The tetragonal Nd-Fe-B alloy structure has a high uniaxial magnetocrystalline anisotropy, which gives the compound a high resistance to demagnetization and a very high saturation magnetization. In an Nd-Fe-B alloy three phases can be defined: the matrix is made of a ferromagnetic tetragonal Nd₂Fe₁₄B phase (φ -phase) and is surrounded by intergranular regions containing a neodymium-rich phase (ρ -phase) Nd₅Fe₂B₆ [12–15] and a B-rich phase (η) Nd_{1+x}Fe₄B₄ [16,17].

Several studies relate the corrosion properties of these alloys with the magnets microstructure [7–9,18], and others point out the important role played by hydrogen [16,19–21]. 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.

Sugimoto et al. [22] 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 [18]. The ρ -phase on the surface of the magnets reacts with water vapour and oxygen in a hot, humid atmosphere with hydrogen generated from the decomposition of water vapour reacting with the Nd [17]. 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 powdered granules [18]. One of the main causes of loss of coercive field in Nd-Fe-B magnets is regarded to be hydrogen absorption by the φ -phase [19], and the hydrogen decrepitation and corrosion which takes place in the Nd-Fe-B alloys has been attributed to the formation of hydrides [23]. Only few papers have investigated the correlation between the hydrogenation process and corrosion [16,21].

2.2. SmCo permanent magnets

Sintered Samarium Cobalt magnets (SmCo) were the first of the Rare Earth permanent magnet family. RE₂TM₁₇ (Rare-Earth Element and Transition Metal) type magnets originated from the investigation of R₂(Co, Fe)₁₇ alloys in 1972 [24]. Commercial SmCo magnets have a standard formula Sm₂(Co, Fe, Cu, Zr)₁₇ but they are divided into two grades [25].

The microstructure of the Sm₂Co₁₇ alloys has been extensively characterised by several authors [26–28]. It consists of Sm₂Co₁₇ cells of the order of 100 nm in size surrounded by boundaries of SmCo₅, 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 μ m across and interspersed with 2–5 μ m particles of Sm oxide formed during alloy production [29].

Pagnell et al. [29] heated two grades of SmCo magnets (one standard grade and one “high temperature” grade) at temperatures between 300 and 600 °C, for up to 1000 h at the lower temperatures and up to 350 h 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 10–15 μ m after 300 h at 600 °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 Co₃O₄ just below it. The thickest corrosion-produced layer, just above the underlying alloy, was CoFe₂O₄. The oxides appeared to be layered in order of their thermodynamic stability (i.e. CuO/Co₃O₄/CoFe₂O₄) [29].

2.3. AlNiCo permanent magnets

Alnico magnets were developed in the 1930's and were the first “Real” performance permanent magnets. McCaig [30] used the term Al-Ni-Co to describe all permanent magnets based on the Al-Ni-Fe system. 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%). Their magnetic anisotropy and consequently coercive field are due to shape anisotropy arising from a dedicated columnar microstructure favoured by the metallurgical process. AlNiCo permanent magnets are considered being very stable and usually do not require protective coating, unless exposed to salt water or strong alkali solutions because they contain some free elemental iron and so may be prone to surface corrosion.

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