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Corrosion and expansion of grouted Magnox

J. CRONIN[1,]* AND N. COLLIER[2]

[1] National Nuclear Laboratory, Sellafield, Seascale, Cumbria CA20 1PG, UK.
[2] National Nuclear Laboratory, 5th Floor, Chadwick House, Warrington Road, Birchwood Park, Warrington, Cheshire WA3 6AE, UK

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ABSTRACT

With potential storage of several hundred years underground in a geological disposal facility (GDF) before closure, there is a requirement for radioactive waste packages to perform adequately. Over the past 25 years, cementitous grouts based on blast furnace slag (BFS) and ordinary Portland cement (OPC), have been used in the UK to immobilize intermediate-level waste (ILW), Magnox swarf, and currently such wasteforms are in surface storage awaiting geological disposal. Magnox fuel cladding will slowly corrode when encapsulated in alkaline cementitious grouts to produce hydrogen gas and an expansive corrosion product. Expansive corrosion products may lead to degradation of the wasteform and, if extensive, could affect the container. This study investigated the acute and chronic rates of corrosion of unirradiated Magnox swarf encapsulated in a BFS/OPC grout over a range of temperatures (25, 40, 60, 75 and 90ºC) for curing times of up to 2½ years. Structural product degradation starts to develop as the tensile strength of the grout is approached by the expansive forces generated. Deformation of some experimental containers was also noted. An estimate of the time taken for a grouted product to fracture from this study due to the corrosion solely of Magnox is 350 years for storage at 25ºC. Although not fully described in this paper, the main cement phases were calcium silicate hydrate, portlandite and gehlenite; the main product of Magnox corrosion was brucite. The curing temperature did not affect the compositions of the Magnox metal, corrosion product or grout.

KEYWORDS: corrosion, expansion, Magnox swarf, grout.

Introduction

THE original specification for waste packages produced by the Magnox encapsulation plant (MEP) at Sellafield was designed to allow a storage period of 50 years above ground followed by 50 years below ground prior to closure of a geological disposal facility (GDF). However, it is now envisaged that a decision on closure of a GDF will be taken by future generations leading to the possibility of several hundred years storage prior to closure. This extended timescale carries the risk that some of these waste packages may not perform adequately for this period. This potentially represents a very large liability as, in some cases, it may result in a need to retrieve and repackage. Therefore, the impact of long-term Magnox corrosion on the evolution of such waste packages needs further research (Nuclear Decommissioning Authority, 2010).

The aim of this project has been to determine the rates of corrosion of Magnox encapsulated in a BFS/OPC grout in a series of small-scale trials and to relate the corresponding dimensional changes in the cemented product to the corrosion that has occurred. The work has consisted of measuring the rate of chronic corrosion of grouted Magnox over a range of temperatures and to measure the expansion and expansive force generated by the Magnox samples as a function of corrosion over a 2½ year curing period. At end of curing, core samples taken enabled character-

* E-mail: jim.c.cronin@nnl.co.uk
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ization of the corrosion products at the Magnox/grout interface (Cronin and Collier, 2011).

Magnox corrosion

Magnox Al80 is predominately an alloy of magnesium and aluminium (aluminium content 0.7–0.9%). When encapsulated in a cement matrix, Magnox metal reacts with residual pore liquor:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$$

The initial relatively high 'acute' corrosion rate can last for several days and then begins to decline as the ability of the cement to provide water for corrosion reduces. Through intermediate rates of indefinite timescale the corrosion rate finally reaches a steady long-term 'chronic' rate. To monitor the corrosion process, the increase in hydrogen gas pressure per unit time was converted to a mass of Magnox corroded using the ideal gas law. Corrosion data are presented as 'μm yr^{-1}' or as wt.% Magnox corroded; the surface area of the Magnox swarf was taken as 1 $m^2\ kg^{-1}$.

Experimental

Trials were performed utilizing different sized cement grouted products designed to monitor the corrosion and the expansive properties of cement grouted Magnox swarf products at elevated temperatures. The preparation of these products simulated closely the conditions experienced by Magnox swarf encapsulated in the MEP to ensure the products had realistic voidage and total water content replicating MEP operating experience. A SD4 colloidal high shear mixer was used to prepare infill grout at the MEP reference grout formulation (3.44:1 BFS/OPC, water/solid 0.35) and Magnox swarf was prepared by splitting new whole unirradiated Magnox fuel cans that had not been exposed to water.

Where increase in hydrogen gas pressure was used to monitor Magnox swarf corrosion at elevated long term curing temperatures, the cemented products, 15 l volume (nominal dimensions 265 mm diameter and 268 mm height), were prepared in gas tight stainless steel cylindrical lidded containers. Lid furniture consisted of a gas pressure transducer, a thermocouple and automatic and manual gas release valves.

The containers were loaded with dry Magnox swarf (30 to 60 mm in length) equivalent to a loading of 155 kg per 555 l MEP drum volume and covered with sodium hydroxide (pH 10) to condition the Magnox swarf for at least 24 hours. The Magnox swarf was dewatered down to known heel liquor volumes before each container was near filled with cement grout under controlled vibration.

To ensure that infill grout had hydrated under realistic but controlled conditions and that early Magnox corrosion had stabilized to a steady chronic rate to provide comparable cemented products for long term corrosion monitoring at elevated curing temperatures, all products were initially cured at 25ºC. This initial curing time took between 86 and 200 days, after which it was judged that stable corrosion rates had been measured for at least 40 days before long term curing temperature was increased to a pre-determined setting at 25, 40, 60, 75 or near 90ºC. Trials incorporating 15 l cemented products were completed in triplicate. At curing temperatures near 90ºC, Magnox corrosion was monitored using purged airflow directed through an in-line electrochemical hydrogen gas sensor (supplied by GDS Technologies Ltd) with detection range, 0–2000 ppm hydrogen.

Figure 1 shows a container prepared for corrosion monitoring employing the gas pressure increase technique complete with insulated

FIG. 1. Container prepared for Magnox swarf corrosion monitored (hydrogen gas pressure increase technique).

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heating jacket. Cylindrical cement grouted products (3 l volume, nominal diameter 165 × 155 mm height) were also prepared using the same infill and vibration techniques employed for the larger scale cemented products using steel moulds. Upon retrieval from the moulds these products were placed unrestrained in containers prepared for corrosion monitoring and measurement of either dimensional change, or placed within a load cell assembly for measurement of longitudinal and circumferential expansive forces. To confirm that the grout infill technique used had prepared void-free grouted products for all trials, a 3 l product cured at ambient temperature was later sliced for internal inspection. Figure 2 shows a photograph of the sliced 3 l void free product.

Characterization of the Magnox/grout interface and the corrosion products

Core product samples (2 inch diameter) taken from selected containers representing the range of long term curing temperatures were taken for measurement of thickness, elemental composition, morphology of the corrosion layer and surrounding metal and grout using environmental scanning electron microscopy (ESEM) with energy dispersive analysis by X-ray (EDAX). The ESEM analysis was performed using a FEI Quanta 200 Mark 2 Field Emission Gun fitted with an Oxford Instruments Inca 250 energy dispersive X-ray (EDX) spectrometer.

Mineralogical characterization of the corrosion products and the grout at the interface was performed using X-ray powder diffractometry (XRD) to determine the composition of any crystalline material present using an INEL Equinox 1000. Thermogravimetric analysis (TGA) of the grout at the Magnox/grout interface and from the bulk of the matrix to provide data on the free and bound water content of the grout at the end of corrosion monitoring was performed using a NETZSCH STA409PC thermal analyser.

FIG. 2. Sliced 3 l void free product.

Magnox corrosion and dimensional change

Six cement grouted products (3 l) were prepared for corrosion monitoring using the pressure increase technique with the unrestrained products retrieved at specified curing times for visual inspection, weighing and dimensional measurement.

Magnox corrosion and expansive forces

Six cement grouted products (3 l) were prepared for corrosion monitoring using the pressure increase technique with measurement of expansive forces. In these trials each product was sandwiched between two circular steel plates with the upper plate supporting a load cell (5000 kg capacity) bearing down onto the surface of a cemented product to measure the longitudinal compressive force generated during corrosion. In addition, a clevis pin type load cell (1000 kg capacity) was strapped around the circumference of each product to measure the corresponding circumferential expansive force. Figure 3 shows a load cell assembly complete with a restrained 3 l product.

Results

Magnox corrosion

Although not shown graphically, at the end of the initial curing period at 25ºC, the steady corrosion rates measured for the larger scale, 15 l products, were 0.19 to 0.59 μm yr^{-1}. At elevated temperatures, enhanced corrosion rates approaching 3000 μm yr^{-1} were measured before corrosion rates steadily declined to reasonably similar steady chronic corrosion rates. Table 1 presents acute and chronic Magnox corrosion rates measured at temperature for 15 l, gas pressure trials.

Figure 4 shows the total Magnox swarf corroded under the four temperature curing conditions maintained for the larger scale, 15 l products, where corrosion was monitored using the pressure increase technique. The mass of Magnox swarf corroded after curing for near 900 days at 25ºC is 0.1 to 0.26 wt.%, whereas at 75ºC between 10.3 to 30.8 wt.% original Magnox swarf had corroded. Similar profiles derived from three

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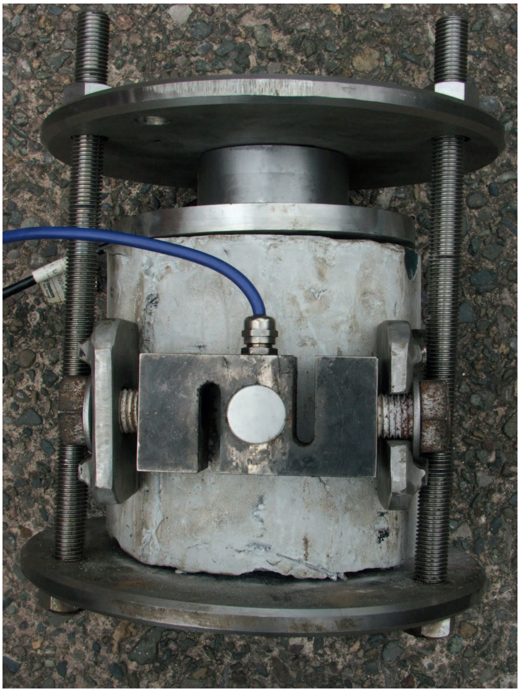

FIG. 3. Load cell assembly with restrained 3 l product for measurement of expansive forces.

gas sensor trials that were maintained at a higher temperature near 90ºC (~87ºC) for a period of time, provided products with 14.7, 21.8 and 28.2 wt.% Magnox swarf corrosion.

Figure 5 shows an Arrhenius plot that compares Magnox corrosion rate data from this study with corrosion rate data from a substantial number of trials carried out in the UK using Magnox swarf or fin in saturated cement grout systems (Cronin and Collier, 2010; Hoch *et al*., 2010). It is seen that the two datasets are closely aligned.

Two Arrhenius corrosion rate equations are shown on the plot. The first equation was derived from all the corrosion rate data generated by this study:

$$\text{Ln Corrosion rate } (\mu\text{m yr}^{-1}) = -14748/T\text{ (K)} + 47.273 + \text{Ln}(4997390) \quad (1)$$

Whereas the second Arrhenius corrosion rate equation was that taken from historic data combined with all the corrosion rate data generated from this study:

$$\text{Ln Corrosion rate } (\mu\text{m yr}^{-1}) = -13362/T\text{ (K)} + 27.489 + \text{Ln}(4997390) \quad (2)$$

The replacement of Ln(4997390) with Ln(871045) in each rate equation shown above converts the corrosion rate from m^3 h^{-1} m^{-2} to wt.% per year. The standard deviation associated with equation 2 is 0.84. This standard deviation was derived from several hundred historical measurements that considered variables such as BFS/OPC ratio, temperature, water content, Magnox form and whether Magnox used was unirradiated or radiated. The Arrhenius rate equation as given in equation 2, has been used in conjunction with the product expansion force and corrosion rate data to predict MEP type product storage times.

Magnox corrosion: dimensional change

Corrosion rate data measured during long term curing at 60ºC, and later at 75ºC, are consistent with those measured at larger scale with between 2 and 8 wt.% total Magnox swarf being corroded. Figure 6 shows a 3 l product with 7.2 wt.% Magnox corroded.

For the six products prepared the extent of cracking and product degradation steadily increased with the extent of Magnox corrosion. For products that remained intact with no

TABLE 1. Magnox corrosion rates measured at temperature for 15 l gas pressure trials.

Trial temperature (ºC)	Chronic Magnox corrosion rate at end of initial curing period at 25ºC (μm yr^{-1})	Highest acute Magnox corrosion rate measured at elevated curing temperature (μm yr^{-1})	Chronic Magnox corrosion rate measured at end of trial (μm yr^{-1})	Total Magnox corroded at end of trial (wt.%)
25	0.19–0.59	–	0.21–0.50	0.12–0.26
40		1.2–2.8	0.80–1.6	0.39–0.69
60		7.7–29	7–28	1.9–5.9
75		324–2791	31–134	10.3–30.8

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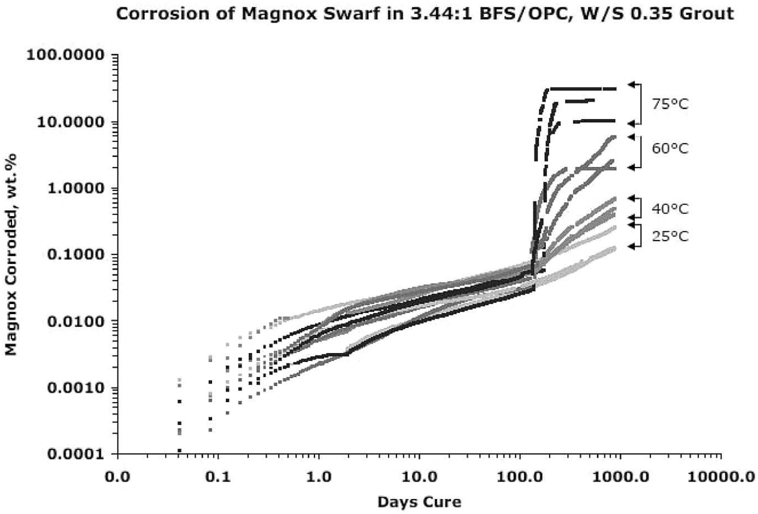

FIG. 4. Corrosion of Magnox swarf in BFS/OPC grout at different temperatures.

significant external cracking, no expansion above the limit of detection (~1 mm) using a micrometer was measured.

Magnox corrosion: load cell expansion

A steady increase in longitudinal expansion force was measured as Magnox corrosion progressed at the elevated long term curing temperature of 60ºC. No significant circumferential expansion was measured. Long term corrosion rates were comparable to those measured for other cemented products cured long term at 60ºC although higher cumulative Magnox corroded values approaching a maximum of 34 wt.% Magnox corroded was achieved.

The longitudinal expansion profiles were characterized by a steady, more or less linear,

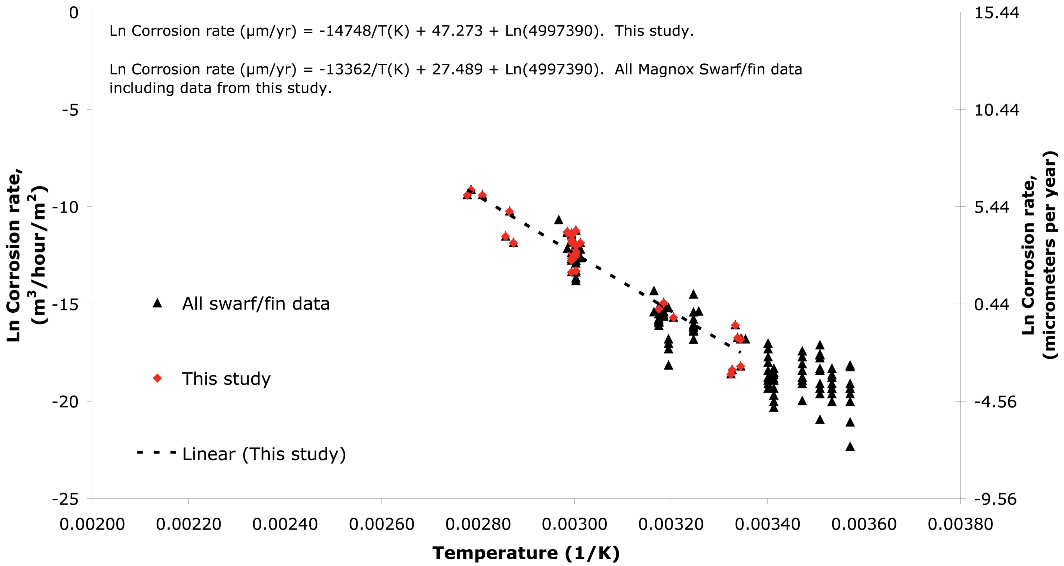

FIG. 5. Arrhenius relationship between Magnox corrosion in grout and reciprocal temperature.

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FIG. 6. A 3 l product at 7.2 wt.% Magnox corroded.

increase in expansion as corrosion proceeded, until about 5–10 wt.% Magnox had corroded. Thereafter, the profiles became erratic as corrosion continued to higher levels; this is probably indicative of the beginning of structural degradation in the restrained products.

Figure 7 shows typical longitudinal force *vs.* Magnox corrosion profile generated in this study. Linear trend lines fitted suggests that the unit increase in longitudinal force per wt.% Magnox corroded, before product degradation starts to develop, generally lay between 0.14 and 0.47 MPa per wt.% Magnox corroded where an average (typical) rate is calculated to be 0.33 MPa per wt.%. The magnitude of the longitudinal forces experienced by the products suggests that the total expansive stresss of 1.2 to 2.6 MPa at which structural degradation starts is related to the tensile strength of the cement grout. This is expected to lie between 1 and 4 MPa and previous measurements on cemented Magnox swarf samples (100 mm cubes) has determined tensile strength to be between 2 and 3 MPa.

Magnox corrosion: effect on the waste package

Using equation 2 the data can be used to estimate storage time until an MEP wasteform fractures (i.e. it exceeds the product tensile strength). The assumptions are as follows: cure temperature 25ºC, tensile strength 3 MPa, tensile strength development 0.33 MPa per wt.% Magnox corroded and a corrosion rate of Magnox derived from equation 2 of 2.62×10^{-2} wt.% per year.

Table 2 shows calculated storage times at 25ºC for an MEP type product to fracture. Times are shown for a cement matrix having tensile strengths of 2, 3 and 4 MPa and for average and upper and lower bound calculated corrosion rates. The estimate of the time taken for a typical MEP product to fracture due to the corrosion solely of Magnox is calculated to be about 350 years for storage at 25ºC using best estimates of corrosion rate and expansive force and a grout tensile strength of 3 MPa. However, depending on values taken for the rate of corrosion, the tensile strength

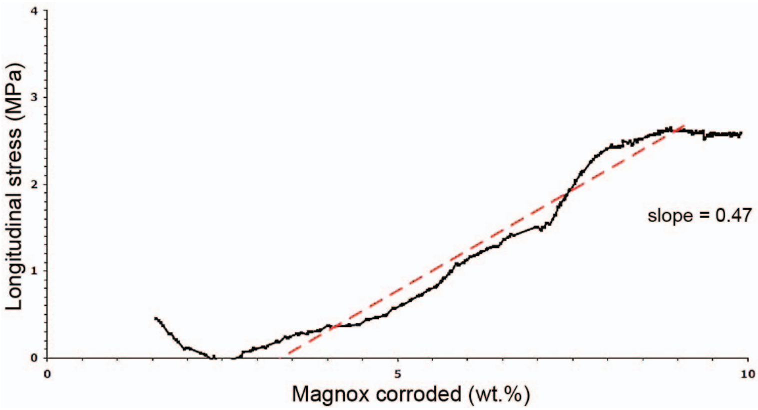

FIG. 7. Profile of expansive stress against Magnox corroded.

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TABLE 2. Product storage times before product fracture (25ºC).

	– Lower bound expansion force(0.14 MPa per wt.%)			– Typical expansion force (0.33 MPa per wt.%)			– Upper bound expansion force(0.47 MPa per wt.%)		
	Years								
Assumed tensile grout strength	Lower	Mean	Upper	Lower	Mean	Upper	Lower	Mean	Upper
	Magnox corrosion rate: 2.62×10^{-2} wt.% per year; SD = 0.84								
2 MPa	2927	545	102	1242	231	43	872	162	30
3 MPa	4390	818	152	1863	347	65	1308	244	45
4 MPa	5854	1091	203	2483	463	86	1744	325	61

of the grout and the expansive forces generated as a result of corrosion, the onset of the product cracking could range between about 30 and 5800 years. It should also be noted that the MEP product stores are ventilated but not temperature controlled and the average annual ambient temperature is below 25ºC.

Containers maintained at curing temperatures of 75ºC were noted to have suffered notable distortion at end of curing; the container bases had become slightly domed and containers walls had notable expansion and undulations along their lengths.

A ‘waste package’ comprises a ‘waste form’ in a ‘waste container’. UK nuclear industry guidance (NDA Industry Guidance, 2011) is concerned with the ability of the waste package to fulfil a range of safety functions such as containment of inventory under normal operating conditions and under accident conditions. Waste package failure is defined in the context of these safety functions. Mechanical fracture of a waste form does not necessarily imply waste package failure, but the reduced performance of a fractured waste form may contribute to failure, or potential failure to satisfy one or more safety functions.

Characterization of Magnox/grout interface and corrosion products

Figure 8 shows a backscattered SEM image and associated EDX trace for a product sample cured at ~87ºC. The EDX results for the Magnox metal showed no difference in elemental composition resulting from the increase in curing temperature, with magnesium being the principal element detected.

The principal elements detected by EDX in the corrosion layer of all samples were magnesium and oxygen with XRD analyses strongly suggesting the presence of brucite, $Mg(OH)_2$. The quantity of aluminium appeared to be only very small. There was no elemental evidence to suggest that different phases were forming in the corrosion layer due to differences in the curing temperature. Little chemical interaction was observed between the Magnox corrosion product and the cement phases other than some indication that a small amount of the magnesium had combined with cement through the presence of hydrotalcite. Thermogravimetric analyses showed that the reduction in Magnox corrosion rate measured after curing for 100 days or less at the two higher curing temperatures, 75 and ~87ºC, was due to these samples reaching very low or negligible free water contents.

Conclusions

Acute and chronic corrosion rates have been determined for Magnox swarf encapsulated in BFS/OPC grout at curing temperatures of 25, 40, 60, 75, and up to 90ºC. These data show that up to 200 days cure at 25ºC is required for the initial acute corrosion phase to decline to provide measurement of steadier longer term chronic corrosion rates.

Characterization of the samples has provided confidence that the swarf was well infilled during the grouting process and given that the preparation of the products closely reflected that carried out in the Magnox Encapsulation Plant at Sellafield, the samples are considered to be closely representative of Magnox swarf encapsulated by MEP. The chronic rate of Magnox corrosion over the temperatures examined has proved to be compatible with Magnox corrosion datasets obtained from other sources and this indicates that these data are representative of Magnox swarf behaviour in grout.

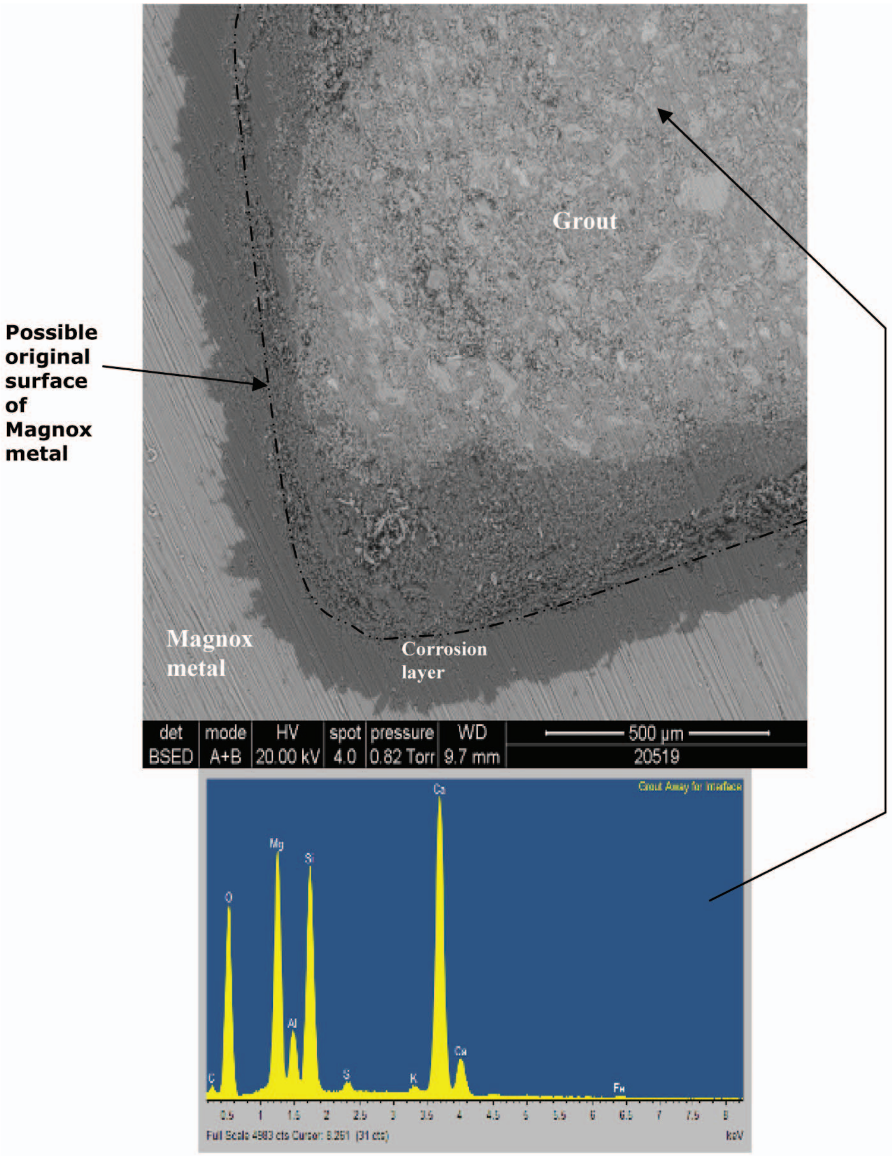

FIG. 8. A backscattered SEM micrograph and associated EDX trace for a product sample cured at ~87ºC.

The load cell expansive trials indicate that structural product degradation starts to develop as the tensile strength of the grout, typically 1.2–2.6 MPa is approached. An expansive stress generation rate of 0.14–0.47 MPa per wt.% corrosion could be used in modelling of the effects of corrosion product expansion on wasteforms. A best estimate of the time taken for a typical MEP product to fracture due to the corrosion solely of Magnox is about 350 years for storage at 25ºC. However, depending on the values chosen for the rate of corrosion, the tensile strength of the grout and the expansive forces generated as a result of corrosion, the onset of the product cracking could range between about 30 and 5800 years.

No expansion above the limit of detection of about 1 mm, as measured with a micrometer was measured in the 3 l unrestrained grouted samples.

The deformation of the container caused by Magnox corrosion at curing temperatures of 75ºC or above may be useful in validating expansion models.

Although not presented in this paper, the main phases formed in the grout during curing are calcium silicate hydrate and portlandite with minor quantities of gehlenite. The main component of the corrosion product is brucite. The effect of curing temperature did not affect the composition of either the Magnox metal, corrosion product or grout.

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