Characterization of Radioactive Wastes Incorporated in a Cement Matrix

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Abstract

The incorporation of radioactive material in cement mixtures is a commonly used procedure for conditioning various kinds of low- and medium-active waste streams. The resulting solid products are non-combustible, sufficiently radiation resistant, and exhibit reasonable mechanical strength as well as chemical and thermal stability. In order to learn more about the underlying mechanisms responsible for the fixation of the radio-elements, phase characterization studies have been performed. Main interest was focussed on the question of whether cesium and strontium show mineralization, and thus improve their leachability resistance. It could be shown that both elements appear to be just more or less uniformly distributed in the gelatinous filled pore spaces. Improvement of Cs and Sr leach rates is mostly due to sorption phenomena on selected additives, but more important, it depends essentially on the degree of porosity of the cementitious products.

Résumé

L'incorporation de matériel radioactif aux mélanges de ciment est une méthode utilisée couramment pour le conditionnement de divers types d'effluents de faible et de moyenne activité. Les produits solides qui en résultent présentent une tenue suffisante aux rayonnements, une résistance mécanique raisonnable ainsi qu'une stabilité chimique et thermique. Des études de caractérisation des phases ont été effectuées afin de mieux comprendre les mécanismes sous-jacents responsables de la fixation des radioéléments. L'intérêt principal a porté sur la question à savoir si le césium et le strontium présentent un état de minéralisation, ce qui améliorerait leur résistance à la lexiviabilité. Il a pu être prouvé que les deux éléments semblent distribués plus ou moins uniformément dans les pores remplis de matière gélatineuse. L'amélioration des taux de lixiviation du césium et du strontium est principalement due au phénomène de sorption se manifestant chez certains additifs, et dépend essentiellement du degré de porosité des produits de cimentation.

Introduction

The method generally considered for the permanent disposal of nuclear waste is to incorporate the radioactive material into a solid, which is then placed in a geological repository. The solid is made of waste and nonradioactive additives, with the formulation selected to produce a durable solid that will minimize the potential for dispersal of the radionuclides.

Cement mixtures are widely used as matrices for the immobilization of low- and medium-active wastes. Cement has many favourable characteristics that have contributed to its popularity as a radioactive waste fixation matrix [1]. The required solidification technology is rather simple. The resulting solid products are noncombustible, strong, radiation-resistant, and have reasonable chemical and thermal stability.

A disadvantage of concrete is its low thermal conductivity, which makes it unsuitable for high-activity wastes, where the heat deposition is appreciable. Also gas generation due to radiolysis may cause problems.

The waste form must be considered as one part of a total nuclear waste disposal system. Its primary role within this system is to provide the initial barrier against radionuclide release. Emphasis is focused on reducing the availability of the waste radionuclides to water leaching when the wastes are disposed of in a repository. Current policy on long-term waste isolation is that the waste package, which includes the waste form and the canister, should provide a complement to the natural geological barrier until the waste hazard has been greatly reduced by radioactive decay. Most important with regard to safety aspects is the operational time of a repository. In the post-closure phase, product integrity is of less importance, since in the long term the natural geological barriers will provide radionuclide retention.

Keywords: radioactive waste management, leaching, cesium, strontium, cement, radiation stability, mechanical stability, morphology, fission products.

The major issues regarding the application of cement-based waste forms to radioactive waste management problems are

1. leachability;
2. radiation stability;
3. mechanical stability;
4. phase complexity of the matrix; and
5. effects of the waste stream composition.

A cursory state of the art review is given for items 1 and 2, whereas a detailed presentation of experimental results is included for the other issues.

Leachability

Leach rates of radionuclides from the solid cementitious waste product indicate the important parameter: quantity of radioactivity as a function of time that is available for dispersal. However, one has to distinguish between two different mechanisms:

1. corrosion of the cementitious waste product, and thus uniform disintegration of the solid; and
2. element-specific dissolution of radioelements by selective leaching.

Considering a simple corrosion attack in salt brine, different processes are involved:

- the intrusion of chloride ions into the pore system of the cement stone;
- leaching-out of nitrate ions;
- interchange of Ca^{++} for Mg^{++};
- corrosive attack due to the formation of $CaSO_4$ phases;
- true dissolution of radionuclides.

This whole process does not necessarily involve a complete dissolution, and thus a mobilization of the disintegration material. Part of it may be truly dissolved, whereas the rest may just exist in a dispersed state. Because of the prevailing fairly high pH value, many ions form insoluble oxyhydrates. Only the radionuclides present as dissolved iogenic species are mobilized by liquid transport phenomena. The dispersed fraction is much less mobile.

The corrosion process obeys a $\sqrt{t}$-law. An important parameter affecting the corrosion rate is the water to cement value (w / c). The lower the ratio w / c, the better the corrosion stability. The parameter most likely responsible for the observed effect is the increasing porosity with increasing w / c-value, measured between 0.27 and 0.50. This observation is in agreement with the finding that low-porosity cementitious products obtained using blast-furnace or high-alumina cements exhibit a higher corrosion stability.

In the presence of brines containing sulphate (e.g., Q-brine), the cement products swell under the formation of gypsum phases or double salts like $Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$, $Mg_2(OH)_3Cl \cdot 4H_2O$. However, no ettringite formation, $Al_2(SO_4)_3 \cdot 6\,Ca(OH)_2 \cdot 26\,H_2O$, has been observed, which normally adversely affects the compressive strength of the product.

Table 1: Leach Rates of Different Nuclides from Portland Cement Products in Q-Brine Applying the IAEA Test at 20°C [2]

Nuclide	$R_L [g \cdot cm^{-2} \cdot d^{-1}]$
Cs	$1 \cdot 10^{-2} - 1 \cdot 10^{-3}$
Sr	$5 \cdot 10^{-3} - 5 \cdot 10^{-4}$
Co	$2 \cdot 10^{-4} - 2 \cdot 10^{-5}$
Ru	$1 \cdot 10^{-4} - 2 \cdot 10^{-5}$
Pu	$1 \cdot 10^{-5} - 1 \cdot 10^{-6}$

Q-Brine Composition: 63% H_2O, 34% $MgCl_2$, 2% $MgSO_4$, 0.6% KCl, 0.2% NaCl.

The concept of leach rates quantifies the rate at which water or brine attacks the matrix of the cement stone matrix. The leach rate (R_L), which is a function of time, is defined as

$$R_L = \frac{m_l \cdot w}{m_t \cdot S \cdot t} \, [g \cdot cm^{-2} \cdot d^{-1}] \qquad (1)$$

where

m_l = amount of a specified nuclide leached during the test duration;
m_t = amount of the specific nuclide initially present in the test specimen;
S = geometrical surface area of test specimen for cement product;
w = weight of test specimen;
t = duration of test.

Selective leaching experiments yield element-specific leach rates. The incremental leach rate decreases rapidly with $1/\sqrt{t}$ at the beginning. This phase may be described by a diffusion-controlled mechanism. After a period of a few hundred days the leach rate becomes constant. Typical leach rate values for Q-brine are listed in Table 1.

Radiation Stability

Cementitious waste products contain a fairly high amount (20–30%) of water, which is either distributed in pores or bound in the various hydrated phases. Gas production by radiolysis, and thus pressure build-up, may therefore become an important safety consideration. The problem could even be enhanced by the decomposition of nitrates present in most of the solidified materials.

Although some experimental results for hydrogen, oxygen, and nitrous oxide formation are available [3, 4], the necessary information is still insufficient. More data are required to evaluate the consequences arising from radiolytic interactions. It seems, however, that no harmful nitrous oxides, especially N_2O, are formed in even nominal quantities. Mostly hydrogen is produced, and also, in the presence of nitrate, smaller amounts of oxygen. Nitrate salts reduce the hydrogen production by factors of 3 to 10, depending on the nitrate percentage in the product due to secondary reactions consuming hydrogen atoms. The radiolysis gas is easily released from the cementitious waste product. Therefore, no serious structural damage (e.g., by crack formation, etc.) should take place as a consequence of internal gas pressure build-up.

Typical values for gas formation (10–30% $NaNO_3$ content) are

H_2:0.3 – 0.8 ml / kg·10^6 rad; and

O_2:0.1 – 0.2 ml / kg·10^6 rad.

As one would expect from theoretical considerations, alpha radiolysis is more effective, by a factor of 2 to 3, than gamma radiolysis.

Mechanical Stability

Mechanical stability is primarily concerned with compressive strength of the cementitious products. The surface area of the waste form is also an important parameter in minimizing the leach rate. Measurement of compressive strength can provide important additional information about the quality of the immobilized waste conditioned for disposal. A minimum compressive strength of 2.5 N / mm^2 (= 25 bar) is recommended in Germany. The values obtained are dependent on several factors, such as cement formula, salt content, and composition, additives, and water-to-cement ratio. The dependence of the compressive strength on the water / cement ratio can be deduced from the values in Table 2.

Increasing nitrate contents reduce the compressive strength of the cementitious waste forms. However, these products can tolerate quite high nitrate loadings, as can be deduced from Figure 1.

A drastic reduction of the bending strength of the cementitious waste products occurs if they are exposed to brine, particularly Q-brine. The effect is already observed after several days to a few weeks. Although no alteration is visible on the face of the product body, bending strength may have decreased below the limiting value of about 2 N / m^2. At the fractured edges liquid drips out.

The effects of addition of detergents on hydration capability have been assessed, since waste waters to be treated very often contain such chemicals in considerable quantities. Only a minor influence of C_3S degradation has been observed, but a remarkable retardation occurs in the case of C_3A. Because the leach rates are related by the degree of hydration of the cement, longer curing times are required. However, the longer-term leach rates remain relatively constant, supposing the porosity is not changed considerably by the action of the detergents.

Table 2: Compressive Strength of Immobilized Medium-Active Waste Concentrate as a Function of the Water-to-Cement Ratio (Portland Cement, PZ 55), Curing Time 20–28 Days, Dry Salt Loading ≈ 25%

Water / cement ratio	*Compressive strength N / mm^2*
0.35	14.5
0.40	10.8
0.45	7.2
0.50	5.4

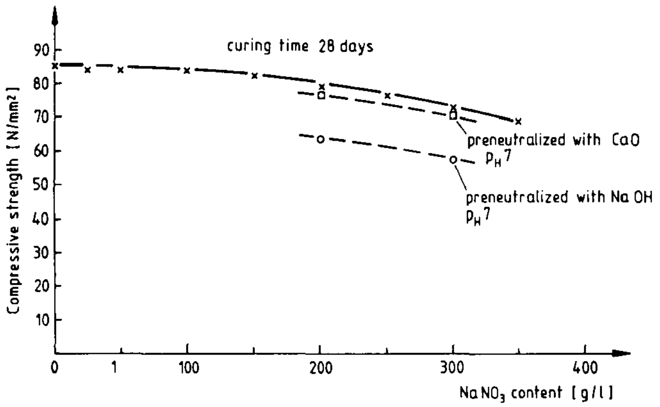

Figure 1: Dependence of compressive strength of MAW cement products on sodium nitrate content. Standard samples prepared according to DIN 1164, PZ 55; water / cement ratio = 0.45.

The results obtained may be summarized as follows:

1. The compressive strength decreases with increasing water-to-cement ratio.
2. Also, the compressive strength decreases with increasing salt loading of the product.
3. The leach rates increase slightly with decreasing compressive strength.
4. Increasing porosity of the cementitious waste form has a strong effect on its compressive strength; increase of porosity from 3 to 10% reduces the compressive strength to approximately 50% of its original value.

An effective way to improve products is by polymer impregnation [5]. It not only increases mechanical stability by approximately two to three orders of magnitude, but, still more advantageously, improves leaching resistancy. Leach rates are improved by factors of 10^2–10^3, at least in the short term.

The procedure consists of mixing the waste with cement and allowing it to solidify at ambient temperature. Afterwards, a catalyzed organic monomer, like styrene, is poured over the surface of the concrete block and allowed to soak in. The pores are thus filled up with the plastic, yielding a low-porosity product. In the course of heating at low temperatures (50–70°C), a polymer-impregnated concrete body is formed. In addition, the polymer forms a thin surface over the top of the material.

Morphology of Cementitious Waste Products

A question of utmost importance with regard to product quality is: What chemical compounds are formed in cement products containing the radioactive nuclides? In the present investigation, attention was focused on the radio-elements strontium and cesium. Are they built in to new stable mineral phases, or are they just more or less uniformly distributed in the amorphous gelatinous pore spaces?

It is known that the pore fluid in a set cement is not pure water, but a solution containing high concentrations of alkaline compounds [6]. The strongly alkaline nature of the micropore solution depresses the solubility of calcium and strontium but does not markedly affect the solubility of cesium, which remains high. A large number of fission product elements (e.g., rare earths, zirconium, actinides, as well as iron and cobalt) form insoluble oxides or hydrous oxides, which remain comparatively insoluble in an alkaline environment. The measured leach rates (see Table 1) are in agreement with these facts.

Cement matrices characteristically exhibit poor retentivity for species that are soluble in alkaline environments. A typical example of this kind is the alkaline element cesium, whereas strontium shows a distinctly stronger retention. Despite their high specific surface area, the hydration products of cement have virtually no sorptive capacity for cesium, and only a poor one for strontium.

In order to learn more about the underlying mechanisms responsible for the fixation of the radio-elements, phase characterization studies have been performed. The influence of the medium-active waste composition (e.g., salt load, complexing agents, etc.) was investigated. Important parameters with regard to cement hydration and reactivity are the degradation rates of the phases:

Ca_3Al (tricalcium aluminate = responsible for settling of the cementitious paste), and

Ca_3Si (tricalcium silicate = responsible for the product strength).

They have been measured by applying X-ray diffraction analysis. Some of the results are shown in Figures 2 and 3.

It is obvious that CaO is a much more suitable reagent for the degradation / hydration of Ca_3Si and Ca_3Al. Since sodium acts as a cement poison, which becomes evident by the reduced hydration ability, its addition should be minimized or, even better, totally omitted. A considerable increase of Cs and Sr leachability is the logical consequence. It appears that the immobilization of the radionuclides inversely correlates with the calcium hydroxide present in the hydrated cement matrix.

Main interest was focused on the question of whether cesium and strontium show mineralization, and thus improve their leachability resistance by a molecular-disperse fixation. The microstructure investigations were carried out with a scanning electron microscope (SEM), coupled with X-ray disperse spectrometry (EDS). In addition, transmission electron microscopy (TEM), coupled with EDS and electron microprobe analysis (EMP), were employed.

Neither method succeeded in identifying a mineralized Cs or Sr phase. All Cs and Sr are retained in the gelatinous pore spaces. Chemical analyses of the pore water, and in addition X-ray diffraction investigations, revealed that strontium is solely present in the form of $SrSO_4$. For cesium, no separate Cs-phases were traceable. Pore water analyses indicated that this element only subsides as $CsNO_3$.

Figure 4 shows a SEM picture of the pore space matrix. The images reveal the interior of the monolithic

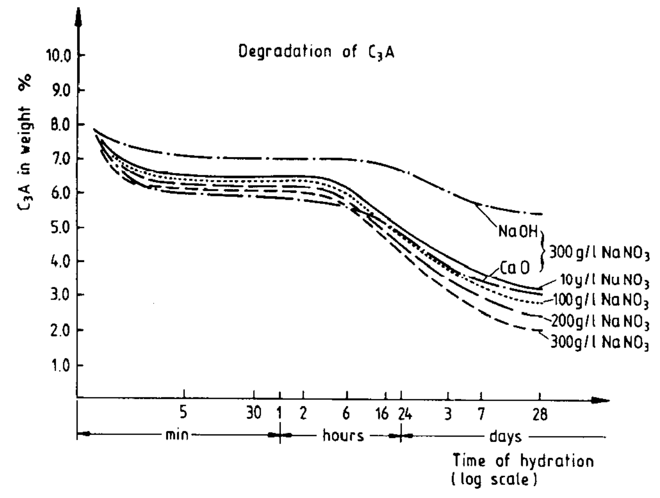

Figure 2: Influence of sodium nitrate content in MAW on hydration of cement; degradation of C_3A phases. Influence of pre-neutralization, either with NaOH or CaO.

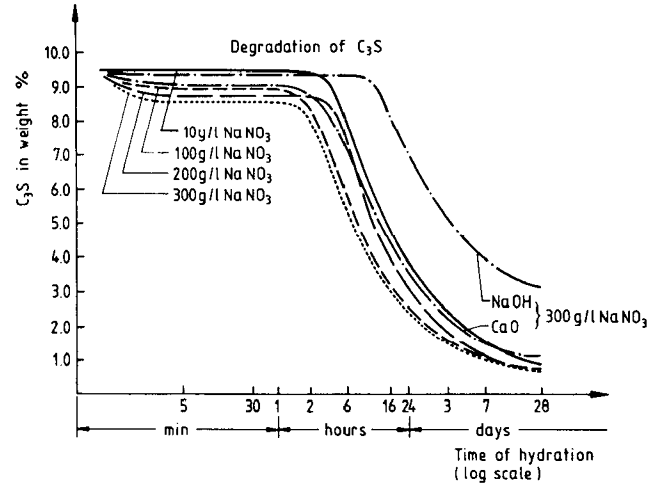

Figure 3: Influence of sodium nitrate on cement (e.g., degradation of C_3S phases. Pre-neutralization, either with NaOH or CaO.

Figure 4: Inner pore space of a cementitious product; w/c ratio 0.34; $CsNO_3$ 50 g/l.

Figure 5: Globular $CsNO_3$ precipitation in the pore space matrix.

form, but no new crystalline phases of Sr or Cs. The bright parts indicate a Cs enrichment. A non-uniform Cs enrichment is typical if either a K or Na enrichment is also observed. It is well known that these two elements can substitute Ca in the pore spaces, as can Cs. In a few cases, a globular Cs enrichment could be detected, as is shown in Figure 5. It indicates a $CsNO_3$ precipitation. The existence of the Cs enrichment was proved by applying X-ray backscattering (Figure 6).

Conclusions

It turns out that cements and concrete can serve merely as physical barriers for cesium and strontium. No new crystalline phases, besides the plain carbonate, nitrate, and sulphate compounds, could be detected.

It could be shown that the improvement of cesium and strontium leach rates is mostly due to sorption phenomena on selected additives, but, more important, on the degree of porosity of the cementitious products. In fact, the leachabilities of the nuclides are essentially diffusion-controlled.

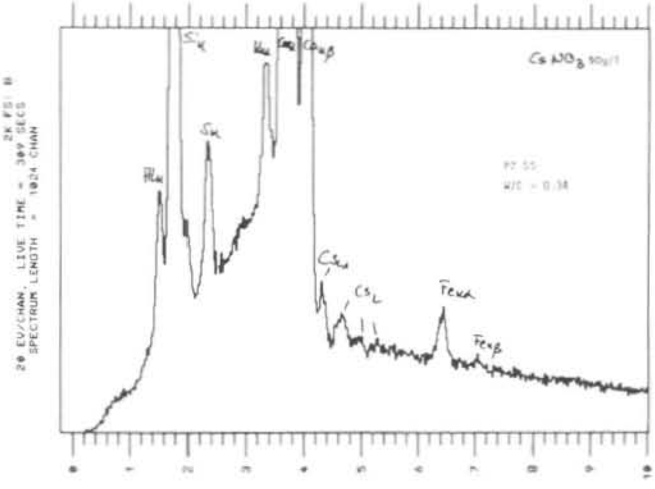

Figure 6: X-ray backscattering diagram of pore space matrix; $L_{\alpha 1}$ line at 4.3 kV.

Improvement of cesium and strontium retention may be achieved in two ways:

1. Increase of the sorption characteristics of the matrix by incorporating substances that possess significant
   - sorption surface-active material (e.g., from blast furnace slag, natural pozzolan, active SiO_2, coal combustion fly ashes);
   - structure-active material capable of forming mineral phases. However, so far no really effective substance has been found.
2. Alteration of the physical properties of the cementitious waste form by the addition of cement modifiers, or utilization of alumina-rich cements. For example, the addition of high surface SiO_2 leads to extensive changes in the microstructure. The most important matrix parameters with respect to leaching are total porosity, pore size and distribution, and pore interconnectivity.

An improvement in the pore size distribution and a decrease of open porosity is best achieved by the employment of modified cement formulations with a high alumina content. Increasing the sorptive capacity by adding surface-active material like bentonite can be counterproductive in that it causes higher porosity.

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