New Binders, New Trends, New Potentialities in Waste Cementation – 15095

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ABSTRACT

It has long been common practice to solidify and stabilize low- and intermediate-level radioactive wastes with calcium silicate cements (ordinary Portland cement, or composite cement). However, wastes produced by nuclear activities are very diverse and some of their components may chemically react with cement phases or mixing water, reducing in some cases the quality of the product. This paper reviews the potential of three kinds of alternative inorganic binders to treat problematic wastes: (i) calcium aluminate and sulphoaluminate cements, (ii) magnesium and calcium phosphate cements, and (iii) alkali-activated binders. Their setting and hardening process is briefly presented, and their potential for waste conditioning is discussed and illustrated. The opportunity offered by these new binders opens a wide field of research which should be attractive and stimulating both for physico-chemists and nuclear industry in the years to come.

INTRODUCTION

Cementitious materials intended for radioactive waste solidification and stabilization usually include substantial amounts of calcium silicate cements (ordinary Portland cement (OPC), or composite cement) [1]. Calcium silicate cements benefit from technology transfer from civil engineering research, and also from more than 150 years of experience on its durability under various service environments.

However, wastes produced by nuclear activities are very diverse and some of their components may chemically react with cement phases or mixing water, reducing in some cases the quality of the product. These reactions, such as adsorption, precipitation, acid-base or redox reactions, can result in inhibition, retardation or acceleration of the cement hydration process. In some cases, the chemical interactions between waste and cement proceed slowly without affecting hydration, but eventually result in the deterioration of the waste form in storage or disposal, for instance by swelling and cracking. The usual strategy to reduce or eliminate adverse waste-cement interactions consists in turning the penalizing constituent(s) of the waste into a form which is thermodynamically stable in cement. One alternative to avoid such a pre-treatment, which increases the complexity and cost of the process, would be using a binder showing a better chemical compatibility with the waste than OPC, i.e. materials which provide a function that OPC-based materials cannot achieve.

At the same time, Portland cement manufacturing industry is under close scrutiny these days because of the large volumes of CO_2 emitted by this industry: tremendous quantities of cement are produced (about 4Gt in 2013) and the expectation from society for alternative solutions increases. Alternative binders, designed in order to have a lower carbon footprint or to process unused resources by the cement industry, are progressively emerging worldwide and will be largely available tomorrow when the waste produced today will have to be stabilized. The cement paradigm is currently moving from single universal cement based on OPC to an array of cement types (calcium aluminate or sulfoaluminate cement, alkali activated materials, Mg-based binders, supersulfated cements…).

Considering these new binders extend the field of application of cementation in the context of radioactive waste stabilization and their potential for waste stabilization / solidification has to be discussed. This paper reviews the potential of three kinds of alternative inorganic binders, divided for clarity reasons into three categories, depending on whether they are based on (i) hydration reactions (sulphoaluminate cements), (ii) acid-base reactions (magnesium phosphate cements) or (iii) polycondensation reactions (alkali-activated binders and more specifically geopolymers).:

CALCIUM SULPHOALUMINATE CEMENTS (CSACs)

What are CSACs?
The first calcium sulphoaluminate cements were developed in Russia and Japan in the 1960s and were first tested at industrial scale in China in the 1970s. Their production exceeded 1 million tons in 1999 [2], and has stayed stable around 1.2 ~ 1.3 million tons since 2004 [3], i.e. a relatively low level due to the high cost of bauxite, one of the raw materials used.
CSA clinker is produced by firing mixtures of limestone, gypsum and bauxite of appropriate compositions in shafts or rotary kilns, as for OPC clinker, but at a lower temperature (1200-1300°C) [4]. Industrial by-products or waste materials can be advantageously added to the blend to reduce the cost of the clinker. The clinker is then interground with calcium sulphate in much higher content (typically 15-25 weight % of gypsum [5]) than for OPC (a few weight %). By varying this content, a series of materials, ranging from rapid-hardening to shrinkage compensating, and eventually to self-stressing, can been designed [5], with applications for construction by cold weather, urgent repair, precasting, self-levelling mortars and screeds [6], glass-fiber reinforced cement composites [7]...
CSACs can have highly variable compositions, but all of them contain ye'elimite, also called tetracalcium trialuminate sulphate $C_4A_3\underline{S}$[1], in their clinker [8, 9]. In sulphoaluminate belite clinkers, ye'elimite predominates over belite, the second predominant phase [10, 11]. Other secondary phases may also be present, depending on the composition of the raw constituents [12]. In the presence of iron oxide in the raw meal, a small amount of this oxide may enter into the structure of ye'elimite, giving the solid solution $C_4A_{(3-x)}F_x\underline{S}$, with x around 0.15 [11, 13]. In addition, the ferrite phase ($C_2(A, F)$) may be formed, leading to the so-called ferrialuminate clinkers. The calcium aluminate phases CA and $C_{12}A_7$ may also be present if the SO_3 content in the raw meal is insufficient to convert the whole amount of Al_2O_3 into ye'elimite. On the contrary, anhydrite ($C\underline{S}$) remains in the clinker in free form at too high SO_3 contents. Free lime may also be encountered in some clinkers.

Tables I and II provide a comparison of the oxide and phase compositions of OPC and CSACs.

TABLE I: Typical oxide composition (weight %) of OPC clinker and CSA clinker.

	Al_2O_3	CaO	SiO_2	Fe_2O_3	SO_3
OPC clinker	3 - 8	59 - 67	17 - 25	0.5 - 6	-
CSA clinker	8 - 47	36 - 61	3 - 27	1 - 13	3 - 15

TABLE II: Typical phase composition of OPC and CSAC (sulphoaluminate belite cement).

	Primary phases	Secondary phases
OPC	C_3S	C_2S, C_3A, C_4AF, $C\underline{S}H_2$
CSAC	$C_4A_3\underline{S}$, C_2S, $C\underline{S}/C\underline{S}H_2$	C_4A_F, C_2AS, $C_{12}A_7$, CA, CT

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[1] Shorthand cement notations: C = CaO, A = Al_2O_3, S = SiO_2, $\underline{S}$ = SO_3, F = Fe_2O_3, H = H_2O, T = TiO_2

Hydration Process

Hydration of CSACs occurs according to dissolution – precipitation process. The hydration reactions and equilibria in CSACs are complicated and not as well defined as for OPC. The hydration of ye'elimite depends on whether calcium sulphate and calcium hydroxide are also present [10, 14, 15] (Table III).

In pure water, ye'elimite is postulated to yield calcium monosulphoaluminate hydrate and aluminium hydroxide as products of hydration (Eq. 1).

Mixes of ye'elimite and gypsum produce aluminium hydroxide together with ettringite if the molar ratio between the two reactants is at least 1:2 (Eq. 2), or a mixture of ettringite and calcium monosulphoaluminate hydrate if the amount of gypsum is reduced (Eq. 3).

Mixes of ye'elimite and calcium hydroxide yield hydrogarnet and AFm phases in the absence of gypsum (Eq. 4), while ettringite is the sole product if sufficient amounts of calcium hydroxide and gypsum are present (Eq. 5).

TABLE III: Balance equations postulated to describe the hydration of ye'elimite [10].

Balance equation	Eq. n°
$C_4A_3\underline{S} + 18\ H \rightarrow C_3A.C\underline{S}.H_{12} + 2\ AH_3$	(1)
$C_4A_3\underline{S} + 2\ C\underline{S}H_2 + 36\ H \rightarrow C_3A.3C\underline{S}.32H + 2\ AH_3$	(2)
$2\ C_4A_3\underline{S} + 2\ C\underline{S}H_2 + 52\ H \rightarrow C_3A.3C\underline{S}.32H + C_3A.C\underline{S}.H_{12} + 4\ AH_3$	(3)
$C_4A_3\underline{S} + 7\ CH + 2x\ H \rightarrow C_3AH_6 + 2\ C_3A.\ ½\ C\underline{S}.\ ½\ CH.xH$ (approximate composition)	(4)
$C_4A_3\underline{S} + 8\ C\underline{S}H_2 + 6\ CH + 74\ H \rightarrow 3\ C_3A.3C\underline{S}.32H$	(5)

Depending on the clinker composition, additional hydrates may precipitate, such as strätlingite (C_2ASH_8), C-S-H, CAH_{10} (a metastable product) or siliceous hydrogarnet [16].

Applications for Waste Conditioning

– **Cementation of heavy metals or borate ions**

Due to the different cement chemistries, the rate of hydration of CSAC may be less affected by strong retarders of OPC such as heavy metals or borate ions.

For instance, ashes resulting from the incineration of technological wastes with neoprene and polyvinylchloride may contain substantial amounts of soluble zinc chloride [17], leading to potential concentrations as high as 0.5 to 1 mol/L in the mixing solution. Zinc is known to have deleterious effects on OPC hydration. Setting is strongly delayed, and can even be inhibited at high zinc loadings [18], while hardening is slowed down [19]. To reduce this adverse interaction, the classical approach is to perform a chemical pre-treatment of the waste, aiming at precipitating Zn(II) as a phosphate, silicate or calcium compound [20]. An alternative consists in using a CSAC, which is much less retarded than OPC, as shown by Berger et al. [21] (Figure 1). The waste can thus be solidified without any pre-treatment.
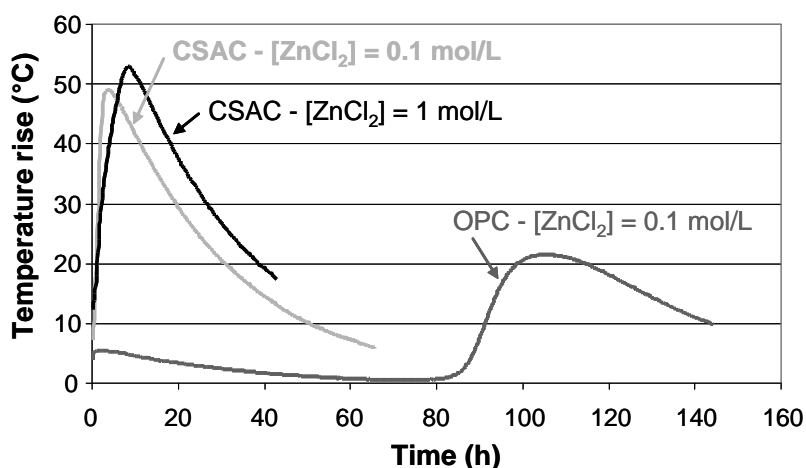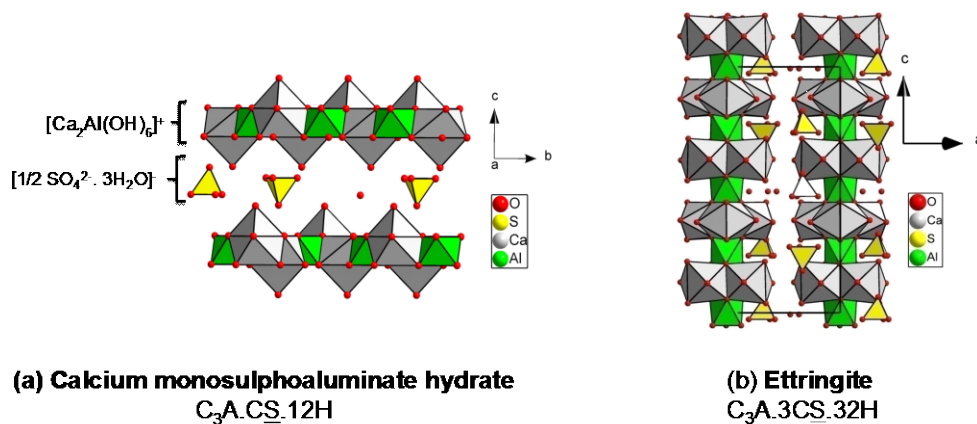
Figure 1 : Comparing the hydration rate of CSAC and OPC, obtained by semi-adiabatic Langavant calorimetry, as a function of the initial $ZnCl_2$ concentration in the mixing solution. CSAC prepared from 80% CSA clinker + 20% gypsum.

– **A favourable mineralogy for waste immobilisation**

As for OPC, the high pH of the insterstitial solution and CSACs (from 10.5 to 12.5 [16]) allows the precipitation of many radionuclides as hydroxides.

Moreover, the main hydrates of CSAC are ettringite, an AFt phase which structure is composed of positively charged columns $[Ca_3Al(OH)_6]^{3+}$ arranged parallel to the c-axis, and of negatively charged channels $[3/2SO_4.nH_2O]^{3-}$, and calcium monosulphoaluminate hydrate, an AFm phase, belonging to the lamellar double hydroxide (LDH) with a crystal structure composed of positively charged main layers $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers $[1/2\ SO_4.nH_2O]^-$. These two phases exhibit a rather flexible structure, and can accommodate many substitutions (Figure 2).

(a) Calcium monosulphoaluminate hydrate
$C_3A.C\bar{S}.12H$

(b) Ettringite
$C_3A.3C\bar{S}.32H$

Reported ion substitutions

Al^{3+} site	$Cr^{3+}, Fe^{3+}, Ga^{3+}$
SO_4^{2-} site	$HBO_3^{2-}, CO_3^{2-}, Cl^-, OH^-, Br^-, I^-, NO_3^-,$ $ClO_3^-, IO_3^-, ClO_4^-, MnO_4^-, CrO_4^{2-},$ $Fe(CN)_6^{3-}, S_2O_3^{2-}, WO_4^{2-}$

Ca^{2+} site	$Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$
Al^{3+} site	$Cr^{3+}, Si^{4+}, Fe^{3+}, Mn^{3+}, Ni^{3+}, Co^{3+}, Ti^{3+}$
SO_4^{2-} site	$B(OH)_4^-, CO_3^{2-}, OH^-, CrO_4^{2-}, AsO_4^{3-}, SeO_4^{2-},$ $VO_4^{3-}, BrO_3^-, NO_3^-, MoO_4^{2-}, ClO_3^-, SO_3^{2-},$ IO_3^-

Figure 2: Structure of calcium monosulphoaluminate hydrate (a) and ettringite (b), and possible ion substitutions [22-25 and references therein].

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CSACs have been shown to insolubilize borate ions efficiently [26]. Borates are incorporated in an AFt phase, even with low calcium sulphate content cements. CSACs may also have a potential to stabilize waste streams with significant amounts of chloride and carbonate ions, including ^{36}Cl and ^{14}C long-lived radioactive isotopes. Mesbah et al. [27] have shown that carbonates are rapidly depleted by calcium monosulphoaluminate hydrate to form calcium monocarboaluminate hydrate and/or calcite, depending on the ratio between carbonates and monosulphoaluminate. Chloride ions react more slowly and the final chloride-containing products are Kuzel's salt and/or Friedel's salts, depending on the ratio between the two reactants. CSACs are also interesting binders for conditioning wastes with high levels of sulphates, such as demolition waste containing hydrated plaster [28]. This waste component replaces, at least partly, the calcium sulphate source usually ground with the CSA clinker, and takes part to the hydration process. Concerning cations, and whatever their gypsum content, CSACs have been shown to provide very good confinement of heavy metals such as lead, cadmium, zinc, and trivalent chromium [29-31].

–   **Self desiccation and lower alkalinity of the pore solution**

Aluminium is a reactive amphoteric metal, readily forming a protective oxide layer on contact with air or water. This layer is generally regarded as stable in the pH range 4.5 – 8.5. However, in a strong alkaline solution, such as the pore solution of OPC, the layer is soluble and corrosion continues, with production of dihydrogen, formation of expansive metal hydroxides as well as calcium-based aluminosilicates [32].Using CSAC could lead to a marked reduction in aluminium corrosion as compared with composite OPC system [33, 34] (TABLE IV).

TABLE IV: Aluminium corrosion rates in CSAC and OPC/blast furnace slag (BFS) matrix [34].

Binder	Peak rate during the first 24 h ($L.hr^{-1}.m^{-2}$)	Rate ($L.hr^{-1}.m^{-2}$) at		
		24 h	**4 d**	**40 d**
CSA	0.22	0.010	0.0002	Below detection
BFS:OPC	5.8	0.81	0.10	Not measured

CSA clinker composition: $C_4A_3\underline{S}$ 58%, C_2AS 17%, CA 16%, C_4AF 4%, CT 4%, $C_{12}A_7$ 1%; Cement compositions: CSA : 60 wt% clinker / 40% gypsum at w/c = 0.6; BFS:OPC 90:10, w/c = 0.33; T = 40°C

Some corrosion is detected in the first 24 hours, but, following this initial period, rates fall to very low levels. The interstitial pH of the CSAC matrix, around 11, is lower than that of the BFS/OPC reference (pH around 13), but still outside the range of passivation of aluminium, which could explain the initial corrosion. Subsequently, the binding of a large amount of water into the ettringite structure may lead to self-desiccation of the system, lowering the internal humidity, and thus reducing the ongoing corrosion. Recently, a special grout, compatible with aluminium components, has been designed for the decommissioning of old reactors at Savannah River site (USA). It is based on CAC blended with calcium sulphate (66.6% Fondu + 33.7 % of Plaster of Paris), which hydrates to form ettringite and develops an interstitial solution pH of ~9.5. About 92 m^3 were poured into a reactor vessel at the end of 2010 [35].

MAGNESIUM PHOSPHATE CEMENTS

What are Phosphate Cements?

Phosphate cements are the main representatives of acid-base cements. The setting / hardening process is brought by a reaction between acid and basic compounds, yielding a salt or hydrated salt. The acid reactant may be an inorganic acid, or an acid salt (for example monoammonium phosphate, or acid phosphates and polyphosphates of ammonium and alkali metals). The basic constituent is usually a weakly basic or amphoteric metal oxide with a moderately small ionic radius (MgO, ZnO, CaO). Concerning magnesium phosphate cements, which are usually applied as mortars or concrete mixes for

rapid repair works, their constituents are magnesium oxide (calcined, or "deadburnt", magnesia) and a water-soluble acid phosphate, which is most often diammonium hydrogen phosphate $(NH_4)_2HPO_4$. Struvite $(NH_4MgPO_4.6H_2O)$ is the main product of reaction (Eq. 6), and the one mainly responsible for setting and hardening.

$$MgO + (NH_4)_2HPO_4 + 5H_2O \rightarrow NH_4MgPO_4.6H_2O + NH_3 \qquad (6)$$

Other by-products may also form in unwanted side reactions, and an amorphous or poorly crystalline phase may also be precipitated in mixes with very low water contents [36]. Noxious gaseous ammonia is released in the hardening process, which is not suitable for radioactive waste immobilization. This problem can be avoided by using alkali phosphates (such as NaH_2PO_4, KH_2PO_4, Na_2HPO_4, K_2HPO_4) instead of ammonium phosphate. The counterpart is a decrease in the final strength of the hardened material.

Applications for Waste Conditioning

The potential of magnesium phosphate cements for waste conditioning results at least from three factors: (i) many contaminants precipitates as phosphate of very low solubility, (ii) a low pore solution pH, close to neutrality.
In Argonne National Laboratory (USA), a matrix called ceramicrete was developed to treat problematic low-level mixed wastes [37]. The process is based on a reaction with deadburnt MgO and monopotassium phosphate KH_2PO_4, leading to the precipitation of $MgKPO_4.6H_2O$ (MKP). The reaction is rapid and exothermic. Boric acid (at a typical content of 1 to 2 wt% of the binder) has thus to be used as a retardant to get an acceptable setting time and to limit the temperature rise during setting and hardening. Langton et al. [35] noticed however that a minimum temperature of 65°C is necessary to form a significant amount of MKP. At lower temperatures, other hydrated magnesium potassium phosphate phases precipitate, with no binding power. The solidified binder typically exhibits a compressive strength between 20 and 30 MPa, a density of ~ 1.8 g/cm3, an open porosity of 2-5 vol %, and a pore solution pH within the range 6-8 [38]. Waste immobilization results from two processes: precipitation of many contaminants (in particular actinides) as phosphates with very low solubility, and physical encapsulation in a dense phosphate matrix. Good results have been reported for several types of wastes: low-level debris wastes contaminated by 137Cs [39], 99Tc oxide-containing wastes [40], Pu-containing combustion residues [41], or highly saline effluents [42]. Stabilization of As, Cr and Hg is however difficult. These contaminants may require additional stabilizers, such as a source of sulfides, to decrease their solubility. Besides, sulphates have to be reduced before encapsulation, and immobilization of caesium requires a prior treatment with zirconium phosphate.

Application to the Conditioning of Aluminium

Because of its low pore solution pH which should limit oxidation of aluminium, ceramicrete was selected as a potential candidate for reactor vessel filling in the Savannah River in-situ decommissioning project [35]. A pumpable, flowable, self-leveling slurry was formulated.
On another hand, the influence of inorganic corrosion inhibitors was also investigated. In 1995, Matsuo et al. reported the beneficial effect of lithium nitrate to reduce the hydrogen release due to the corrosion of aluminium in Portland cement [43]. They explained their results by the formation of a protective insoluble layer of lithium aluminate hydrate at the surface of the metal. It has recently been proven that lithium nitrate kept its inhibiting properties in a magnesium phosphate cement paste [44]. When lithium nitrate was added at a level of 2 wt% (with respect to the mass of $MgO + KH_2PO_4$), the amount of released hydrogen was less than 2.28×10^{-4} $L.m^{-2}.year^{-1}$.

GEOPOLYMER: AN ALKALI-ACTIVATED BINDER

What are Geopolymers?

Alkali-activated binders are made by mixing solid aluminosilicates, such as fly ash, metakaolin, various clays usually activated by heat or blastfurnace slag, with an activating solution comprising high concentrations of alkali hydroxide (NaOH, KOH) and / or polysilicate ($Na_2O.nSiO_2$, $K_2O.nSiO_2$). The reaction product, formed according to a dissolution/polycondensation process, exhibits an X-ray amorphous network structure and is usually called 'geopolymers' [45].

Geopolymer synthesis chemistry depends on the nature of the solid precursor and alkali activator, and many aspects are not fully understood. However, it is possible to describe a general and simplified process [46]:

- Dissolution of the solid alumino-silicate source by alkaline hydrolysis, consuming water, produces aluminate and silicate species that rearrange in solution to form more stable oligomers.
- Dissolution of amorphous aluminosilicates leads to oversaturation of the solution. The oligomers form a large network by condensation, and a gel-like phase precipitates, exhibiting a high aluminium content (Si/Al ratio ~ 1), which can be attributed to the readier dissolution of aluminium than silicon because the Al-O bonds are weaker than the Si-O bonds. This process releases the water that was consumed during dissolution.
- As the reaction progresses, more Si-O groups in the initial starting material dissolve, favoring the evolution of the initial gel-like phase into a more silica-rich product (Si/Al ratio ~ 2). The connectivity of the network increases. This process of reorganization determines the microstructure and pore distribution of the final material.

The alumino-silicate network bears resemblance to zeolite framework, but is generally lacking in long-range crystalline order and its structure consists of a rather randomly arranged three-dimensional network of corner-linked SiO_4 and AlO_4 tetrahedra. To outbalance the negative charges brought by the presence of AlO_4 tetrahedra, a corresponding number of positive charges, in the form of monovalent or divalent cations, are located in spaces between the tetrahedra, together with some constitutional water. This type of product is described in the literature as N-A-S-H gel.

By selecting appropriate starting materials and by varying the conditions of processing and curing, it is possible to vary the properties of the produced alkali-activated binders over a wide range, and to tailor them to specific requirements [47, 48]. Geopolymers can thus exhibit a wide range of properties, including high compressive strength, low permeability, low shrinkage, fast or slow setting, low thermal conductivity, acid, fire and/or freeze-thaw resistance [49].

Potentials of Geopolymers for Waste Conditioning

– **Heavy metals, alkali-earth and alkali ions**

Geopolymerisation also provides an opportunity to stabilize/solidify hazardous wastes. The mechanisms of stabilization are believed to be physical, due to the low permeability of the matrix, and/or chemical. Several processes can occur, depending on the waste contaminant, such as precipitation as a compound (typically a silicate or hydroxide) of low solubility, or binding into the structure for charge balancing roles. For instance, well-designed geopolymers have been shown to provide good immobilization of lead [50] which is believed to precipitate as Pb_3SiO_5 [51]. Ga and Ge may also substitute for Si or Al in the gel structure [52]. Alkali metals (Li, Na, K, Rb, Cs) are mainly immobilized by acting as charge balancing

cations within the gel [53]. In particular, the insolubilization of caesium by a geopolymer (either made of fly ash or metakaolin) is reported to be much better than by an OPC matrix [54].

Bankowski et al. [55] investigated the leaching of various cationic contaminants from a mixed brown coal fly ash / metakaolin geopolymer. Every s- (Ba, Sr) or p-group (As, Se) element was effectively immobilized by the geopolymerisation process.

– **High Alkalinity of the Pore Solution**

The high alkalinity of the interstitial solution of a geopolymer, at least at early age, is beneficial to reduce the corrosion of Mg alloys, used as materilas for fuel claddings in gas cooled nuclear reactors, like UNGG (uranium natural graphite gas) in France or MAGNOX in Great Britain, compared to OPC. According to Lambertin et al [56], the corrosion density of such alloys in a geopolymer activating solution is one order of magnitude lower than in an OPC pore solution. When the alloys are encapsulated in a geopolymer, the H2 production due to corrosion is 2 to 3 times lower than in the OPC matrix during the first 28 days and galvanic currents densities of Mg-Zr//Steel immerse in these materials are also strongly reduced (Figure 4). Furthermore, the absence of calcium from the geopolymer chemistry, makes the chemistry of this binder more compatible with magnesium corrosion inhibitors such as fluoride [57].
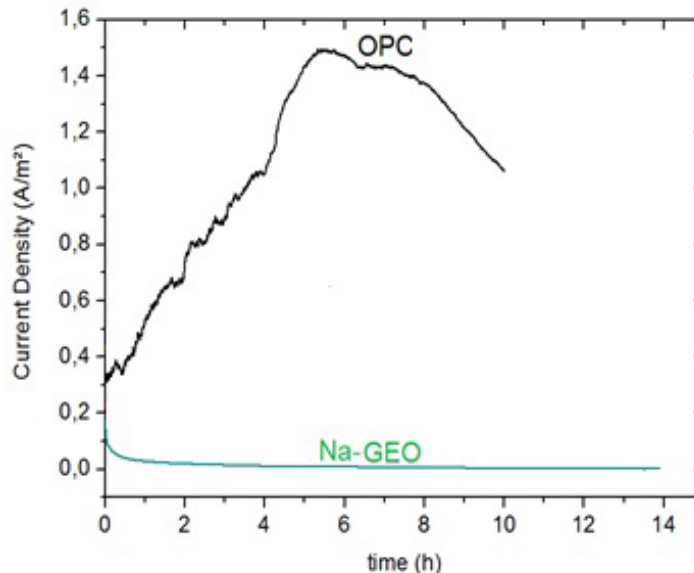

Figure 4: Galvanic currents densities of Mg-Zr//Steel in OPC and sodium-based geopolymer.

On another hand, cement-based solidification/stabilization is considered poorly compatible with organic liquid wastes: many studies reported the effect of organic compounds such as 3-chlorophenol [58] methanol and 2-chloroaniline [59], trichlorobenzene [60] on cement binder and clearly demonstrated that, even at low concentrations, organic materials can produce significant micro-and macrostructural changes to the properties of hydrated material. Usual approach is based on absorption by vermiculite [61] or Nochar[®] polymer [62, 63] followed by a cementation process. In the case of geopolymers, the high salinity of activating solution leads to an increase of the viscosity of liquid phase: it becomes possible to obtain a stabilized emulsion of oil in an alkali silicate solution that can be directly solidified by addition of metakaolin (Figure 5) [64]. Lixiviation tests conducted in pure water on composite material with waste incorporation rate of 20vol% of the final material have shown that after 30 days, the total amount of organic

compounds in the leachate did not exceed 0.19% of the total amount of the initial organic material encapsulated in the sample.
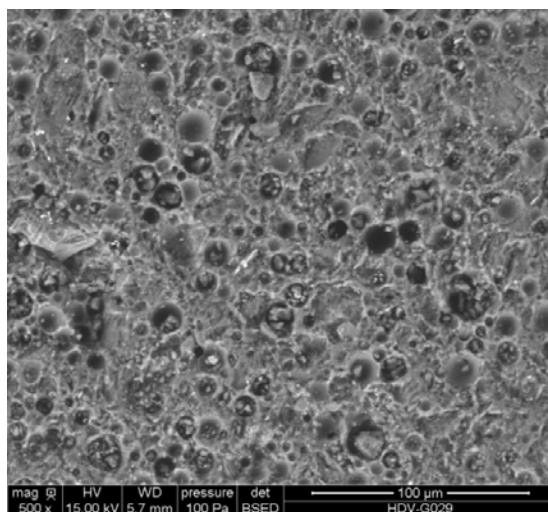

Figure 5: Environmental SEM micrographs of oil/geopolymer composite fractures (20% Vol. of oil and 10 minutes of emulsion stirring).

   – **Alumino-silicate framework**

Some authors suggest that geopolymers may be viewed as amorphous analogs of zeolites or that, from a thermodynamic point of view, geopolymers can be considered as metastable with regard to zeolites [65, 66]. Zeolites are a family of complex aluminosilicates having a three-dimensional network structure containing channels and cavities which can immobilize a variety of contaminants. Controlling the crystallization of geopolymers and tailoring the particular zeolite structures formed may be very attractive to ensure optimal immobilization of the desired contaminants. In this context, materials called hydroceramics have been developed to deal with reprocessing wastes at the Idaho National Engineering and Environmental Laboratory (INEEL, USA) [67]. INEEL waste is characterized by overwhelming amounts of sodium. The matrix constituents include waste (typically 30% dry-mass basis), metakaolin or class C fly ash, ~5% powdered vermiculite (to enhance 137Cs fixation), ~0.5% sodium sulfide (redox buffer and heavy metal precipitant), plus ~10% sodium hydroxide dissolved in enough water to produce a stiff paste. The hydroceramic waste forms are then autoclaved at 90 or 190°C to get a dense matrix with very low solubility, consisting mainly of zeolites.

CONCLUSION

Binders with different levels of development have been presented and Table V tries to summarize the main concerns and remaining key issues for the different investigated binders.
In all cases, the reactions involved in the setting / hardening process are exothermic. While excessive temperature rise is not a problem affecting small-scale laboratory samples, large-volume drums of cemented waste forms may exhibit a substantial temperature rise. This thermal evolution at early age should be taken into account to understand how actual cemented waste forms will perform. The question is all the more important since the solid phase composition in materials based on CSACs, magnesium phosphate and alkali-activated binders depends on temperature.
Besides, understanding the chemistry of cement – waste interactions, and their consequences on the physical properties of the solidified waste forms, including their long-term evolution, will be a critical

task for the acceptance of these alternative binders in nuclear waste conditioning. Particular attention will also have to be paid to their possible interactions with the near-field environment. This offers a wide field of research which should be attractive and stimulating for physico-chemists in the years to come.

TABLE V : Concerns and key issues for the investigated alternative binders.

Elaboration	Magnesium Phosphate cements	Cost and availability of the binders components .Specific surface area of deadburnt MgO can be highly variable from one batch to another, affecting the binder reactivity.
	Geopolymers	Handling of large amounts of highly concentrated solutions..
Heat production	CSACs	Careful management of the initial exotherm is needed.
	Magnesium Phosphate cements	
	Geopolymers	
Setting and hardening	CSACs	CSACs can set very rapidly depending on their ye'elimite content, the kind and content of minor phases, and the amount and reactivity of calcium sulphate. In that case, a retarder (boric acid, citric acid) has to be used.
	Magnesium Phosphate cements	Setting can be too rapid for magnesium phosphate binders, a retarder is then needed.
	Geopolymers	Setting and hardening process highly sensitive to the activation conditions : sometimes, slow strength gain
Durability	CSACs	Hot and dry environments should be avoided for CSACs (ettringite prone to loose water).
	Magnesium Phosphate cements	- Durability unproven
	Geopolymers	Durability to be further considered What is the influence of the geopolymer / zeolite such a transformation on the properties of the matrix?
Interaction with wastes	CSACs	Need for a better understanding of the processes involved
	Magnesium Phosphate cements	
	Geopolymers	

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