Trapping of Nickel and Cobalt in CaNiSi$_2$O$_6$ and CaCoSi$_2$O$_6$ Diopside-Like Phases in Heat-Treated Cement

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Abstract

Niopside (CaNiSi$_2$O$_6$) and copside (CaCoSi$_2$O$_6$), diopside-like phases, were synthesized by ceramizing cementitious hydrates prepared by reaction between Ni- or Co-containing water solution and cementitious mix made of Ca$_3$SiO$_5$ plus SiO$_2$. Both niopside and copside exhibit very low leachability, which shows that these phases have potential for trapping nickel and cobalt, whose certain radionuclides (^{59}Ni, ^{63}Ni, and ^{60}Co) are activation products in metallic structures of nuclear power plants. © 1998 Elsevier Science Limited. All rights reserved

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1 Introduction

1.1 Ceramics through cement ceramization

Pollution by various chemical elements, in particular radioactive elements, is cause for concern. Nuclear waste management is one of the major problems that will face us in the future.[1] Adequate response to nuclear waste management depends on which kinds of wastes are involved. High-level radioactive wastes (HLW) are usually vitrified, whereas medium and low-level wastes (MLW and LLW) are mostly immobilized in cementitious materials. Geological repositories are thought to be the best solution for long-term disposal of radioactive nuclear wastes.

1. Vitrification of HLW offers two advantages. Firstly, glass has a much wider composition chemistry than crystal, which means one given glass can trap various chemical elements. Secondly, the glass fabrication process is less demanding than the ceramic fabrication process. The main drawback of glass, however, is that it is not thermodynamically stable, with consequent potential sensitivity to leaching and vulnerability to radiation and high temperatures.

2. Ceramization allows a noticeable improvement in long-term stability. Synroc[2] is the best known example of such a strategy. A crystal, however, is not as chemically flexible as a glass, which implies that one given ceramic matrix cannot accommodate as many elements as a vitreous matrix. Moreover, the fabrication of ceramics is a complex procedure, in particular because it requires the availability of fine powders. The powder preparation is difficult in the case of radioactive, hazardous materials. Another difficulty arises when natural sintering does not work, in which case one must use complex and costly hot pressing. Till now, comparison between advantages and disadvantages has led to choose vitrification rather than ceramization in France.

3. Cement-based materials for use in nuclear waste repositories will have to fulfill various requirements. In some places, cements will be used for making mechanical barriers, with similar requirements as for conventional building industry. In other places, they could be used for making chemical barriers, which needs high-sorption and low-leachability characteristics, besides resistance to radiation and resistance to medium-to-high temperatures. Even in the case of very special cementitious compositions, however, one cannot expect that porous, hydrated phases offer the

high performance level that is offered by glasses and ceramics, which are materials with strong ionic and covalent bonds, and are impervious, resistant to high temperatures, and thermodynamically stable (in the case of crystallized ceramics). It is the reason why cements and concretes are generally considered as materials for LLW and MLW only, with a limited role with regard to HLW. The present study confirms, however, that cementation-to-ceramization routes have potential for tight trapping of pollutants.

The sophistication of modern separation techniques now allows partial discrimination between chemical elements, which implies that the criticism about ceramics which are less chemically flexible than glasses may not be so severe as it was some decades ago. Moreover, the long-term durability and leachability of nuclear glasses is not comprehensively established. This suggests that ceramization may gain markets if enough efforts are made to simplify the processing procedures and, in particular, to avoid the powder preparation stage.

The route we used[3] allows the synthesis of crystallized ceramic phases by ceramizing a cementitious mix. It is a two-stage route. The first stage consists in making a pollutant-containing water solution react with an anhydrous cementitious mix, to form hydrated phases where the pollutants are immobilized. The second stage consists in heating the green material to ceramize it toward stable, crystallized phases where the pollutants are trapped. By 'immobilization' we mean weak chemical bonding and by 'trapping' tight chemical bonding. A major advantage of the method is that, in many cases, pollutants can be put in water solution, which allows direct reaction between the polluted solution and the anhydrous mix and avoids the needs for pollutant separation and pollutant-containing-powder preparation. Moreover, immobilizing the pollutant in hydrates avoids its dissemination and facilitates its manipulation. A final advantage is that the pollutant is less prone to vaporization during the sintering heat treatment when immobilized in a solid than when dispersed in a powdered state. The method requires that the relevant crystallized phases be located in an equilibrium diagram compatible with cement chemistry. Conventional cements mainly involve calcium silicates (in Portland cements) and calcium aluminates (in high-alumina cements), but one can also use phosphate cements (for the preparation of apatite-based ceramics), or calcium sulphate (plaster of Paris). The limitation imposed by a definite chemistry is not, however, so stringent as one might think. For instance, the ultra-low-cement castables

have demonstrated that only a minute fraction of cement is required to bring cohesion and that many phases can coexist in presence of the elements brought by the cement.

The choice for the phases that have to trap the pollutants is generally suggested by 'natural analogues', that is to say by minerals that have demonstrated their resistance to weathering over geological periods. For instance, the efficiency of cement ceramization was demonstrated by trapping cesium in pollucite, the most stable Cs-containing ore.[3]

The present study was aimed at trapping nickel and cobalt, whose radioactive isotopes are produced by activation of metallic parts in nuclear power plants. The main radionuclides here are ^{59}Ni, ^{63}Ni, and ^{60}Co, but we worked with the corresponding non-radioactive isotopes. This does not address the question of phase resistance to irradiation. However, this issue mainly concerns α emitters, whereas the present radionuclides are β, γ emitters. ^{59}Ni (period: 80 000 years) and ^{63}Ni (period: 100 years) are β emitters; ^{60}Co (period: 5·3 years) is a β, γ emitter, with intense γ emission.

1.2 The systems CaO–SiO$_2$–NiO and CaO–SiO$_2$–CoO

The use of common cement, i.e. Portland cement, leads to the study of systems CaO–SiO$_2$–NiO and CaO–SiO$_2$–CoO, both systems that present similarities with the system CaO–SiO$_2$–MgO.

1.2.1 Nickel-containing materials

The system CaO–SiO$_2$–NiO has an extensive primary field of nickel oxide NiO, a narrow ternary field of nickel olivine Ni$_2$SiO$_4$, and a small ternary field of quaternary CaNiSi$_2$O$_6$. Metasilicate CaNiSi$_2$O$_6$ is the nickel analog of diopside CaMgSi$_2$O$_6$, which explains its name of 'niopside'.[4] Studies about niopside[4–9] have shown that niopside melts incongruently to give nickel olivine plus liquid. The solidus is at 1338°C and the liquidus at 1420°C (in normal atmosphere).[9] Besides niopside, nickel olivine, and nickel oxide, the system CaO–SiO$_2$–NiO was said[10] to contain another phase of potential interest, CaNiSi$_4$O$_{10}$.

1.2.2 Cobalt-containing materials

'Copside' (CaCoSi$_2$O$_6$) is the cobalt analog of diopside[7,11] and CaCoSi$_4$O$_{10}$ was found by Nicolini and Porta[10] in their study of the series CaMSi$_4$O$_{10}$ with M = Mn, Co, Ni, and Cu. CaMnSi$_4$O$_{10}$, CaCoSi$_4$O$_{10}$, CaNiSi$_4$O$_{10}$, and CaCuSi$_4$O$_{10}$ all crystallize in a tetragonal P$_4$/ncc space group with four molecules per unit cell. There are differences in the site symmetry around the central metal atom: CaMnSi$_4$O$_{10}$, CaCoSi$_4$O$_{10}$,

and $CaNiSi_4O_{10}$ have the transition atoms in octa-hedral configuration, whereas $CaCuSi_4O_{10}$ has the copper in either a square-planar coordination or a strongly distorted octahedral coordination. According to Navrotsky and Coons,[11] $CaCoSi_2O_6$ melts incongruently in the temperature range 1150–1205°C, but our own experiments (DTA analysis) have given 1165–1230°C, for a material prepared using the cement route, heat treated at 1200°C for 3 h.

In all ternary systems with CaO, SiO_2, and a divalent transition metal (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}), the diopside structure is encountered when the divalent cation can sub-stitute for Mg^{2+} in octahedral sites. The cation radius must be close to that of Mg^{2+} ($r = 0.66$ Å) and the crystalline field must favor octahedral coordination. The radii are 0·69 Å (Ni^{2+}), 0·72 Å (Co^{2+}), 0·80 Å (Mn^{2+}), 0·74 Å (Fe^{2+}), 0·72 Å (Cu^{2+}), and 0·74 Å (Zn^{2+}). Ni^{2+}, whose electronic configuration is $[Ar]3d^8$ (octahedral symmetry $t_{2g}^6 e_g^2$) and benefits from a high crystalline field stabilization energy ($-6/5\Delta_{octa}$).

Diopside-like crystals[4,9,11,12] are clinopyroxenes, with a monoclinic unit cell where β is close to 106°. Pyroxenes are metasilicates composed of $\{SiO_3^{2-}\}_\infty$ chains formed by sharing $\{SiO_4\}$ tetra-hedra with a periodicity of 2 along the c axis. The chains are stacked parallel and cross-linked by cations, generally in octahedral sites. The cation positions in pyroxenes are of two types. The M_1 sites lie between the apices of opposing tetrahedra, whereas the M_2 sites lie between their bases. M_1 sites are small, almost regular octahedra. M_2 sites are larger, more distorted, and may be either octahedra (when containing a small cation) or 7- or 8-fold coordinated (when containing a large cation). M sites form edge-sharing chains which run parallel to the main silicate chains. In diopside, M1 sites are occupied by Mg^{2+} and M_2 sites are occupied by the larger Ca^{2+}. Si^{4+} cations are located in tetrahedral sites. The three cations (Ca^{2+}, Mg^{2+}, Si^{4+}) surround three unequal oxy-gens, labelled as (1), (2), and (3). Crystal para-meters of niopside and copside are given in Tables 1 and 2.

Table 1. Crystal data for niopside[7]
Monoclinic space group C2/c
a = 9·734(2) Å, b = 8·891(2) Å, c = 5·228(1) Å, β = 105·87(2)°

Atom site	Occupancy	x	y	z
M_1	Ni^{2+}	0	0·90911(6)	0·25
M_2	Ca^{2+}	0	0·29816(1)	0·25
T	Si^{4+}	0·28733(8)	0·09298(9)	0·22752(14)
O(1)		0·1153(2)	0·0861(2)	0·1414(4)
O(2)		0·3603(2)	0·2508(2)	0·3188(4)
O(3)		0·3514(2)	0·0191(2)	−0·0081(4)

(Standard deviation in parentheses).

Table 2. Crystal data for copside[7]
Monoclinic space group C2/c
a = 9·806(1) Å, b = 8·950(1) Å, c = 5·243(1) Å, β = 105·45(1)°

Atom site	Occupancy	x	y	z
M_1	Co^{2+}	0	0·90750(3)	0·25
M_2	Ca^{2+}	0	0·29907(5)	0·25
T	Si^{4+}	0·28727(5)	0·09262(5)	0·23080(9)
O(1)		0·1176(1)	0·0881(1)	0·1473(2)
O(2)		0·3613(1)	0·2487(1)	0·3222(2)
O(3)		0·3508(1)	0·0192(1)	−0·0061(2)

(Standard deviation in parentheses).

It must be noted that diopside, niopside, and copside can be vitrified.[13] In vitreous niopside[14,15] EXAFS and XANES spectroscopy have shown that nickel is mainly in 5-fold coordination.
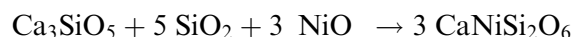
2 Experimental

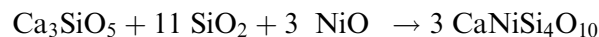Characterization was carried out using XRD, thermal analyses, and leach tests.

2.1 Ni-containing materials

2.1.1 Cement route
Two cementitious mixes were used:

$$Ca_3SiO_5 + 5\ SiO_2 + 3\ NiO \rightarrow 3\ CaNiSi_2O_6$$

and

$$Ca_3SiO_5 + 11\ SiO_2 + 3\ NiO \rightarrow 3\ CaNiSi_4O_{10}$$

NiO resulting from the pyrolysis of a Ni precursor.

Starting materials were pure Ca_3SiO_5 (Lafarge Central Research Laboratory), SiO_2 quartz (Sifraco), and water solution of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (>99%) (Merck), a salt which is very soluble (2385 g l^{-1} at 0°C). Ca_3SiO_5 (mean grain size <10 μm) and SiO_2 (mean grain size ($\cong$2 μm) were ground together in appropriate weight ratio (m[Ca_3SiO_5]/ m[SiO_2] = 0·76 for composition $CaNiSi_2O_6$ compo-sition and 0·345 for composition $CaNiSi_4O_{10}$), then the nickel-containing solution (8·7 mol l^{-1}, which corresponds to 2530 g l^{-1} for composition CaNi-Si_2O_6 and 5·2 mol l^{-1}, which corresponds to 1504 g l^{-1} for composition $CaNiSi_4O_{10}$) was added to the powdered mix (water-to-solid ratio = 0·65). The hydrated mix was then poured into glass tubes sealed with plastic caps and cured at 25°C for 4 days. Then, the consolidated material was extracted and dried at 150°C for 24 h. Heat treatment was carried out in air, with heating rate of 5°C min^{-1} up to 50°C below the soaking
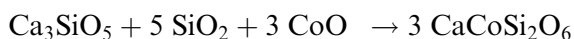
temperature and of $1°C\,min^{-1}$ up to the soaking temperature. Soaking time was of 3 h; soaking temperatures were ranging from 1000 to 1330°C, to be compared with $\approx 1340°C$, which is the melting point of niopside.
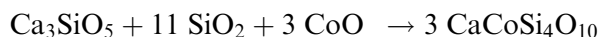
2.1.2 Ceramic route

Besides the cement route, we also used a ceramic route, with $CaCO_3$ (Aldrich Chemical Company), SiO_2 quartz (Sifraco), and cobalt-free anhydrous nickel oxide ($>98\%$) (Rhône–Poulenc) as starting materials. NiO (mean grain size $<2\cdot5\,\mu m$) and SiO_2 (mean grain size $\cong 2\,\mu m$) were ground together, then $CaCO_3$ (mean grain size $\cong 20\,\mu m$) was added. Powder pellets were pressed, then sintered in the same conditions as the cementitious materials.

2.2 Co-containing materials

Only the cement route was investigated:

$$Ca_3SiO_5 + 5\ SiO_2 + 3\ CoO\ \rightarrow 3\ CaCoSi_2O_6$$

and

$$Ca_3SiO_5 + 11\ SiO_2 + 3\ CoO\ \rightarrow 3\ CaCoSi_4O_{10}$$

The cobalt salt (precursor of CoO) was cobalt(II) nitrate hexahydrate ($>99\%$) (Acros Organics). For both compositions ($CaCoSi_2O_6$ and $CaCoSi_4O_{10}$), the concentration of the cobalt-containing solution was $4\cdot6\,mol\,l^{-1}$, which corresponds to $1338\,g\,l^{-1}$. The water-to-solid ratio was higher than for nickel (1·24 for $CaCoSi_2O_6$ and 0·73 for $CaCoSi_4O_{10}$), due to lower solubility of cobalt salt ($1338\,g\,l^{-1}$ at 0°C). Thermal treatments were from 1000 to 1250°C.

3 Results and discussion

3.1 Phase formation

3.1.1 Nickel-containing materials (Tables 3 and 4)
3.1.1.1 $CaO.NiO.2SiO_2$ composition. In materials prepared using the cementitious route, no nickel-containing crystalline phases were observed in non-heat-treated materials. In heat-treated materials, and not taking into account quartz, nickel oxide was the first to crystallize, with wollastonite ($CaSiO_3$) and larnite (Ca_2SiO_4) as minor phases. $CaNiSi_2O_6$ begins to form at about 1000°C, then niopside develops at the expense of other phases. Niopside is the main phase after treatment at 1300°C. At 1330°C, the material is sensibly niopside, although some residues of NiO are still visible, which agrees with results of Raudsepp et al.[16] This temperature is sensibly that of melting, as indicated by our DTA experiments which have indicated that incongruent melting occurs in the temperature range 1320–1380°C. The difference between those results and literature data[9] (1340–1420°C) may be due to difference in materials purity.

The materials prepared using the ceramic route show similar trends to those prepared from cement, although there are slight differences in the proportions of various phases, as shown by comparing the data in Table 3. However, the two routes lead to exactly the same phase contents in materials treated at the highest temperature (1330°C).

3.1.1.2 $CaO.NiO.4SiO_2$ composition. Neither the cementitious route nor the ceramic one allowed us to find any trace of the expected compound $CaNiSi_4O_{10}$. This confirms that niopside is the phase of interest here.

Table 3. X-ray diffraction data, Ni-containing materials

CaO.NiO.2SiO$_2$ composition

Thermal treatment (°C)	$CaNiSi_2O_6$ niopside	$CaNiSi_4O_{10}$	NiO	SiO_2	CaO	$CaSiO_3$ wollastonite	Ca_2SiO_4 larnite
Cement route							
4 days at 25°C then 24 h at 150°C	/	/	/	*** (q)	t	/	/
1000	**	/	***	*** (q)	/	*	t
1100	***	/	***	*** (q)	/	*	t
1200	***	/	***	** (q + c)	/	**	/
1275	***	/	***	* (c)	/	**	/
1300	***	/	*	t (c)	/	*	/
1330	***	/	t	/	/	t	/
Ceramic route							
1000	t	/	***	*** (q)	**	t	/
1100	*	/	***	*** (q)	**	t	/
1200	*	/	***	** (q + c)	/	t	/
1275	***	/	*	* (c)	/	t	/
1300	***	/	t	/	/	t	/
1330	***	/	t	/	/	t	/

/: absent, t: traces, *: low, **: medium, ***: high; (q): quartz, (c): cristobalite, (t): tridymite.

Table 4. X-ray diffraction data, Ni-containing materials

CaO.NiO.4SiO$_2$ composition

Thermal treatment (°C)	CaNiSi$_2$O$_6$ niopside	CaNiSi$_4$O$_{10}$	NiO	SiO$_2$	CaO	CaSiO$_3$ wollastonite	Ca$_2$SiO$_4$ larnite
Cement route							
4 days at 25°C then 24 h at 150°C	/	/	/	*** (q)	/	/	/
1000	*	/	**	*** (q)	/	t	*
1100	**	/	***	*** (q)	/	t	*
1200	**	/	*	*** (q + c)	/	t	/
1275	**	/	**	*** (q + c)	/	t	/
1300	***	/	*	*** (c + t)	/	t	/
1330	***	/	t	** (c + t)	/	/	/
Ceramic route							
1000	t	/	**	*** (q)	*	/	/
1100	*	/	**	*** (q)	*	t	/
1200	*	/	**	*** (q + c)	/	t	/
1275	***	/	*	** (c)	/	t	/
1300	***	/	*	** (c + t)	/	t	/
1330	***	/	t	** (c + t)	/	t	/

/: absent, t: traces, *: low, **: medium, ***: high; (q): quartz, (c): cristobalite, (t): tridymite.

3.1.2 Cobalt-containing materials (Tables 5 and 6)

3.1.2.1 CaO.CoO.2SiO$_2$ composition. No cobalt-containing crystalline phases were observed in non-heat-treated materials. In heat-treated materials, four phases develop at around 1000°C: copside (CaCoSi$_2$O$_6$), Co-akermanite (Ca$_2$Co-Si$_2$O$_7$), cobalt oxide (Co$_3$O$_4$), and cobalt silicate (Co$_2$SiO$_4$). Copside is the main phase in materials treated at temperatures above 1100°C. We have to point out that the materials treated at 1200 and 1250°C were in their domain of incongruent melting.

3.1.2.2 CaO.CoO.4SiO$_2$ composition. Similarly to what was found for Ni-containing materials, we did not find any phase of CaCoSi$_4$O$_{10}$ composition. This confirms that copside is the phase of interest here.

3.2 Leach tests

Leachability was studied for Ni- and Co-based materials prepared by heat-treatments of 3 h at 1275 and 1200°C, respectively. The leach tests were as follows.

Five hundred mg of ground powders (mean grain size < 10 μm) were stirred for 15 min in 20 g of deionized water, then the suspension was stored for 4 days at the selected temperature (50°C or 90°C), with second stirring after 1 day. The containers were made of metal-free polymers. The suspensions were filtered through 0·45 μm cellulose membranes. The leachate pH values were approximately 8·4 for the tests at 50°C and 8·0 for those at 90°C. The leachates were analyzed by ICP emission spectroscopy (Jobin Yvon JY138 Ultrace). For the first analyses, the nickel and cobalt concentrations in leachates were compared to standards with 10·1 ppm of Ni and 9·7 ppm of Co, respectively. However, the leachate concentrations were so small that we moved toward hundred-fold diluted standards (99 ppb of Ni and 97 ppb of Co standards). Moreover, we used the highest voltage that was allowed by the apparatus (990 V). The results were that the nickel concentration remains below 30 ppb and the cobalt concentration remains below 200 ppb. The leaching temperature (50 or 90°C) does not play any significant role. These very low concentrations show that both niopside and copside exhibit excellent resistance to leaching and are, therefore, promising hosts for trapping nickel and cobalt.

Table 5. X-ray diffraction data, Co-containing materials

CaO.CoO.2SiO$_2$ composition

Thermal treatment (°C)	CaCoSi$_2$O$_6$ copside	Ca$_2$CoSi$_2$O$_7$ Co-akermanite	SiO$_2$	CaSiO$_3$ wollastonite	Co$_3$O$_4$	Co$_2$SiO$_4$
Cement route						
4 days at 25°C then 24 h at 130°C	/	/	*** (q)	/	/	/
1000	**	**	***(q)	t	**	*
1100	***	*	* (q)	t	*	*
1150	***	t	t (q + c)	t	t	t
1200	***	t	/	/	/	/
1250	***	/	* (t)	/	/	/

/: absent, t: traces, *: low, **: medium, ***: high; (q): quartz, (c): cristobalite, (t): tridymite.

Table 6. X-ray diffraction data, Co-containing materials

CaO.CoO.4SiO$_2$ composition

Thermal treatment (°C)	CaCoSi$_2$O$_6$ copside	Ca$_2$CoSi$_2$O$_7$ Co-akermanite	SiO$_2$	CaSiO$_3$ wollastonite	Co$_3$O$_4$	Co$_2$SiO$_4$
Cement route						
4 days at 25°C then 24 h at 130°C	/	/	*** (q)	/	/	/
1000	**	*	*** (q)	/	/	/
1150	***	t	*** (q + c)	/	/	/
1250	***	/	** (t)	/	/	/

/: absent, t: traces, *: low, **: medium, ***: high; (q): quartz, (c): cristobalite, (t): tridymite.

4 Conclusion

Ceramizing cementitious mixtures reacted with Ni- or Co-containing water solution is an easy preparation process for obtaining well-crystallized niopside CaNiSi$_2$O$_6$ or copside CaCoSi$_2$O$_6$. Both phases exhibit very low leachability in hot (50 or 90°C) water, which shows that they have potential for trapping nickel and cobalt pollutants in stable solid materials.

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