

Natural sintering of carbonate powder for use as a carbon-14 immobilization matrix

Agnès Grandjean *, Gilles Leturcq

CEA Marcoule, DEN/DTCD, BP 17171, 30207 Bagnols-sur-Cèze cedex, France

Received 1 February 2005; accepted 18 April 2005

Abstract

Carbon-14 generated during fuel irradiation in the reactor is later partially released as $^{14}\text{CO}_2$ during reprocessing. It must not be released directly into the environment because of its long half-life and rapid assimilation by living organisms. The waste volume generated by conditioning depends not only on the type of fuel but especially on the selected conditioning matrix. We propose that a sintered carbonate be used directly as an alternative to cement with the main objective of providing a significant waste volume reduction while ensuring durability equal to or better than that of cement. Many carbonates are difficult to sinter naturally because of their relatively low thermal decomposition temperature. They also exhibit low hardness and are generally friable. We show that a binary carbonate $\text{BaCa}(\text{CO}_3)_2$ yields a sintered carbonate with satisfactory mechanical properties and acceptable water solubility. The carbonate fabrication, pelletizing and sintering conditions are examined and discussed.

© 2005 Elsevier B.V. All rights reserved.

PACS: 81.20.Ev; 81.05.Je

1. Introduction

Carbon 14, a β -emitter, is an activation product generated during fuel irradiation mainly by neutron activation of nitrogen-14 and oxygen-17 in the fuel, the coolant, the moderator and structural materials. In the case of carbide fuel, neutron activation of carbon-13 also produces carbon-14. It is partially released as $^{14}\text{CO}_2$ during spent fuel reprocessing. It must not be released directly into the environment because of its long half-life (5730 years) and rapid assimilation by living organisms.

The waste volume generated by conditioning the resulting carbon-14 depends both on the type of fuel and on the selected conditioning matrix. Irrespective of the nature of the fuel (carbide, nitride or oxide) or the reprocessing technology (hydrochemical or pyrochemical), carbon in the fuel or in the structural elements is eventually found as CO_2 (or, under certain conditions, as CO which is oxidized to CO_2).

Gaseous CO_2 is immobilized by trapping it in carbonate form as BaCO_3 or CaCO_3 [1]. Several matrices are proposed in the literature as capable of immobilizing $^{14}\text{CO}_2$ trapped in carbonate form [2,3]. Examples include:

- Unmodified calcium carbonate in powder form, directly from the trapping process.

* Corresponding author. Tel.: +33 4 66 796 622; fax: +33 4 66 796 030.

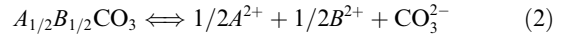
E-mail address: agnes.grandjean@cea.fr (A. Grandjean).

- Carbonate encapsulated in a cement matrix, which is currently the preferred solution considering its low cost, and the safety and compatibility of the process with compounds arising from off-gas trapping (CaCO_3 and BaCO_3).
- Graphite or metal carbides, whose main unfavorable consequences include high fabrication costs and incompatibility with compounds arising from off-gas trapping, requiring prior reduction of the carbonates.

This study explores the possibility of using a massive carbonate as a potential conditioning matrix for ^{14}C trapped in the off-gas stream. The matrix selection criteria are dictated by its performance characteristics:

- *Minimum ultimate wastefrom volume.* Table 1 compares the waste volume generated by various matrices for conditioning 1 kg of ^{14}C . The use of massive carbonate reduces the resulting waste volume by a factor of 3–4 compared with cement.

- *Good chemical stability.* In the case of sintered carbonates, the chemical stability is indicated by the solubility product. Table 2 is a non-exhaustive list of the $\text{p}K_s$ values for the following reactions:



This criterion excludes all the alkali-metal carbonates as potential matrices because of their water solubility.

- *Good thermal stability* indicated by the carbonate decomposition temperature, corresponding to the equilibrium temperature of the $A\text{CO}_3 \rightleftharpoons A\text{O} + \text{CO}_2$ (gas) reaction. The sintering temperature must be below the decomposition temperature to allow natural sintering. The decarbonation temperatures for several simple carbonates (magnesite, calcite, witherite) and mixed carbonates (alstonite and norsethite) produced by the process described below, were determined by laboratory TGA measurements.

Table 1
Waste volume generated for 1 kg of ^{14}C according to selected conditioning matrix

Matrix	Formula	C (wt%)	Waste weight (kg)	Density	Waste volume (dm^3)
Cement	33 wt% CaCO_3	3.96	25.2	2.0	12.6
	33 wt% BaCO_3	2.01	49.8	2.9	17.2
Sintered carbonates	CaCO_3	12.00	8.3	2.71	2.8
	BaCO_3	6.09	16.4	4.3	3.8
	$\text{BaCa}(\text{CO}_3)_2$	8.08	12.4	2.7	3.3
Carbides	SiC	29.96	3.3	3.2	1.0
	WC	6.13	16.3	16.3	1.0

Table 2
Properties of various carbonates

Group	Formula	Name	C (wt%)	Density (g cm^{-3})	Mohs hardness	$\text{p}K_s$ (25 °C)	T_c (°C)
Wegscheiderites	Li_2CO_3	Zabuyelite	16.25	2.09	3	−2.95	
	Na_2CO_3	Natrite	11.33	2.54	3.5	0.59	358
Calcite	CaCO_3	Calcite	12	2.71	3	−8.03	630*
	MgCO_3	Magnesite	14.25	3	4	−7.98	320*
	FeCO_3	Siderite	10.37	3.96	3.5		298
	MnCO_3	Rhodocrosite	10.45	3.69	3		350
	ZnCO_3	Smithsonite	9.58	4.45	4.5		118
	CoCO_3	Sphaerocobaltite	10.1	4.1	3–4		175
	CdCO_3	Otavite	6.97	5.03	3.5–4		291
Dolomite	$\text{BaMg}(\text{CO}_3)_2$	Norsethite	8.53	3.84	3.5		850*
Aragonite	SrCO_3	Strontianite	8.14	3.78	3.5		830*
	BaCO_3	Witherite	6.09	4.31	3–3.5	−8.87	980*
	PbCO_3	Cerussite	4.49	6.58	3–3.5		309
	$\text{BaCa}(\text{CO}_3)_2$	Alstonite	8.08	3.72	4–4.5	−10.6*	600*

T_c is the incipient decarbonation temperature, $\text{p}K_s$ is the solubility product for reactions (1) or (2) depending on the type of carbonate. The data were taken from handbooks, except for values marked with an asterisk (*) which were measured (TGA for T_c , water solubility measurement at 90 °C for $\text{p}K_s$).

- *Good mechanical strength*, indicated by the material hardness. For comparison, chalk is rated at about 3 on the Mohs hardness scale, and a ceramic such as apatite is rated at about 5. Preference is given to carbonates with a Mohs hardness exceeding 3.5.

Based on these criteria, we decided to focus our study exclusively on calcium carbonate, barium carbonate and mixed Ca–Ba carbonate. We propose that a massive carbonate be used directly as an alternative to cement encapsulation with the main objective of providing a significant waste volume reduction while ensuring acceptable chemical durability (low K_s) [4].

2. Experimental procedure

The simple carbonates were obtained directly from commercial powder.

The mixed carbonate $\text{BaCa}(\text{CO}_3)_2$ was synthesized by a room-temperature reaction between Na_2CO_3 dissolved in water and an aqueous solution of CaCl_2 and BaCl_2 in suitable molar proportions. The reaction was instantaneous, forming the desired mixed carbonate (which precipitated) and dissolved NaCl . After solid–liquid separation the carbonate was recovered in powder form, then oven-dried for 48 h at 120 °C. This process is suitable for tests at laboratory scale, but generates aqueous solutions very rich in Na^+ and Cl^- , and is thus not satisfactory for extrapolation to technological scale. Three operating conditions were tested during this study:

- Stoichiometric operation ('S'), in which 1 mol of Ca and 1 mol of Ba were added to 2 mol of CO_3 to obtain stoichiometric $\text{BaCa}(\text{CO}_3)_2$.
- Oversaturation with CO_3 ('SC'), for which the initial Na_2CO_3 concentration exceeded the stoichiometric value. For 1 mol of Ca and 1 mol of Ba, there were 2.2 mol of CO_3 ('SC2.2') or 2.5 mol CO_3 ('SC2.5'). Stoichiometric $\text{BaCa}(\text{CO}_3)_2$ was also formed under these conditions.
- Superstoichiometric Ba ('SB') for which the initial Ba concentration exceeded the stoichiometric value: 0.8 mol of Ca and 1 mol of Ba were added to 1.8 mol of CO_3 ('SB0.2'), or 0.9 mol of Ca and 1 mol of Ba were added to 1.9 mol of CO_3 ('SB0.1'), forming a mixture of stoichiometric $\text{BaCa}(\text{CO}_3)_2$ and BaCO_3 . In case of SB0.2 the mixture is supposed to be 0.8 mol of $\text{BaCa}(\text{CO}_3)_2$ and 0.2 mol of BaCO_3 and in case of SB0.1 the mixture is supposed to be 0.9 mol of $\text{BaCa}(\text{CO}_3)_2$ and 0.1 mol of BaCO_3 .

The X-ray spectrum (Fig. 1) shows that this synthesis route ('S' or 'SB') indeed yields barytocalcite with an excess of barium carbonate in case of superstoichiometric conditions ('SB0.2')

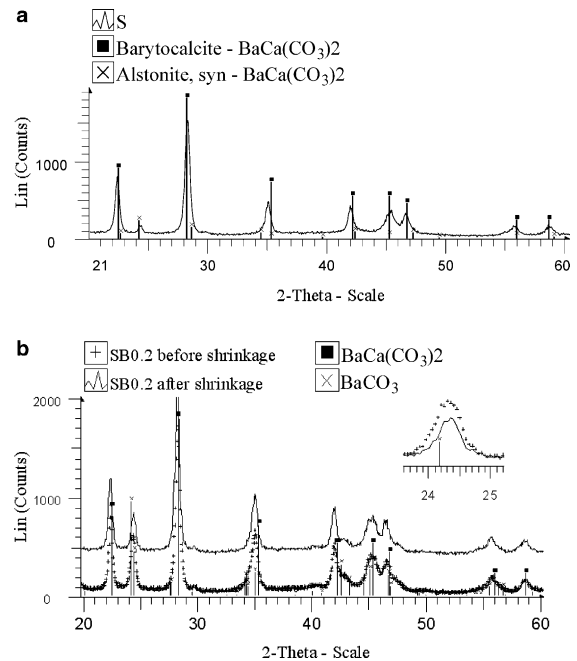


Fig. 1. X-ray spectrum for powder fabricated (a) by the 'S' process (b) and by the 'SB0.2' process before and after sintering.

Other synthesis routes could also be considered. For example, Chang [5] prepared binary and ternary carbonate samples in the desired proportions by a room-temperature reaction between a nitric acid solution of the required cations (e.g. Ba^{2+} and Ca^{2+}) with an aqueous sodium carbonate solution. He also recommended drying the resulting binary or ternary carbonates by precipitation at 110 °C in gaseous CO_2 atmosphere.

3. Results and discussion

3.1. Pelletizing

Pelletizing is an important step toward obtaining high bulk density materials. For the purposes of this study the process was carried out without granulation and without the use of a binder. Under these conditions, we were unable to pelletize commercial BaCO_3 powder. Regardless of the pressure applied, the samples were laminated and cracked. Adding a binder and/or granulating the powder could allow pelletizing. Nevertheless, barium carbonate has low intrinsic hardness (3–3.5) and was therefore not selected as a potentially interesting matrix for natural sintering.

We then measured the impact of the pelletizing pressure on the green pellet bulk density for calcium carbonates and for pure $\text{BaCa}(\text{CO}_3)_2$ or enriched with BaCO_3 . The results are summarized in Table 3. Theoretical

Table 3
Pelletizing and sintering test results

Fabrication conditions	Theoretical density (g cm ⁻³)	Applied pressure (MPa)	Green density (g cm ⁻³)	Temperature (°C)	Time (h)	d/d_{theo} (%)		
S	3.72	75	2.1	580	2	54		
		62	2.04		15	74		
					600	10	^a	
		130	2.46					
		150	2.34					
SC2.2	3.72	15	1.94	580	2	54		
					15	72		
SC2.5	3.72	15	1.97	580	2	55		
					15	72		
SB0.2	3.84	15	1.81	580	2	78		
		15	1.84		15	89		
					600	10	92	
		75	2.17					
		150	2.34					
SB0.1	3.78	15	1.76	580	2	84		
							15	90

^a The pellet was cracked and deformed.

densities in case of ‘SB’ were estimated using these equations:

$$d_{\text{theo}}(\text{SB0.2}) = 0.8d(\text{BaCa}(\text{CO}_3)_2) + 0.2d(\text{BaCO}_3) = 3.84$$

$$d_{\text{theo}}(\text{SB0.1}) = 0.9d(\text{BaCa}(\text{CO}_3)_2) + 0.1d(\text{BaCO}_3) = 3.78$$

The results (Fig. 2) show that for these samples a pressure of 150 MPa was sufficient to obtain green pellets with about 65% of their theoretical density. Granu-

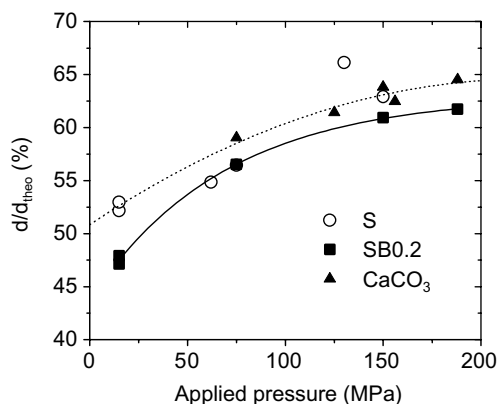


Fig. 2. Effect of pelletizing pressure on green density of the samples.

lation or the use of a binding agent were thus unnecessary to obtain satisfactorily densified green pellets.

3.2. Sintering

The optimum sintering temperature ranges for the materials were determined on the basis of the thermogravimetric (TGA) (Fig. 3) and dilatometry analyses (Fig. 4) for the test carbonates. All the heat treatments applied for the sintering tests were performed with a temperature rise of 100 °C/h to the setpoint temperature, which was maintained throughout the treatment, followed by cooling at 100 °C/h to room temperature.

3.2.1. CaCO₃

According to the literature, calcium carbonate and especially magnesium carbonate are difficult to sinter at high temperature because of their relatively low thermal decomposition temperatures. These findings were confirmed by TGA and dilatometry analyses. Natural sintering of the calcite is clearly impossible, as the temperature at which shrinkage starts (770 °C) is higher than the temperature at which the decarbonation starts (about 630 °C). Yamasaki et al. [6,7] therefore proposed that these carbonates be sintered by high-temperature isostatic press compaction in a hydrothermal medium containing sodium hydroxide. Sintering is thus possible

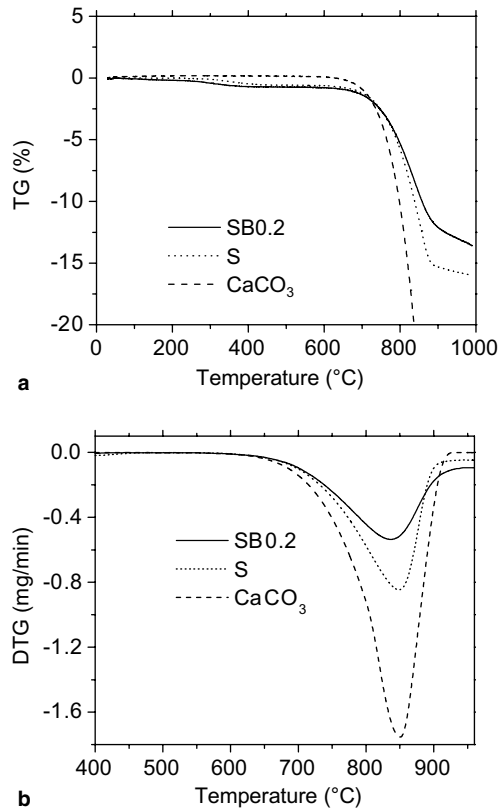


Fig. 3. Thermogravimetric analysis: (a) TG in weight loss (%) and (b) DTG, derivative curve of the TGA.

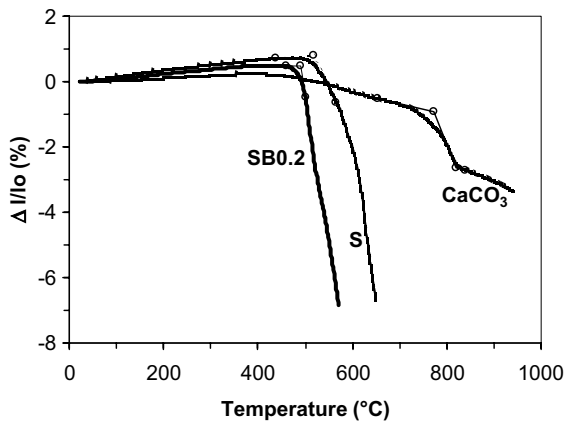


Fig. 4. Shrinkage curves. Heating rate: 3 °C/min.

at low temperatures (<300 °C) under pressures ranging from 25 to 45 MPa.

To obtain dense, compact calcium carbonate pellets by natural sintering, Ishida [8] recommended adding compounds with ionic bonds such as fluorine, lithium phosphate or sodium chloride, for successful sintering

at temperatures below 650 °C. Fujiwaka [9] proposed sintering alkaline-earth carbonates by encapsulating the carbonate powder in a metal matrix and submitting it to a high-temperature heat treatment. The objective of this study is a natural sintering, so we did not perform such procedures.

3.2.2. $BaCa(CO_3)_2$

The sintering tests results obtained for samples ‘S’, ‘SC’ and ‘SB’ are summarized in Table 3. Compared with the stoichiometric mixed carbonate $BaCa(CO_3)_2$, excess $BaCO_3$ proved to be favorable for sintering in several respects:

- *Sintering temperature*: Based on dilatometry measurements, the starting shrinkage temperature of the $BaCa(CO_3)_2 + BaCO_3$ mixture (SB0.2) is lower than that of $BaCa(CO_3)_2$ alone. Thermogravimetric analysis (TGA) showed that the incipient decarbonation temperature is roughly the same for ‘S’ and ‘SB’, about 630 °C. Sintering of $BaCa(CO_3)_2$ (‘S’) powder at 600 °C resulted in a cracked, deformed pellet. Conversely, a pellet densified to 90% was obtained with excess $BaCO_3$ at 600 °C.
- *Densification*: After 15 h of heat treatment at 580 °C, the bulk density of stoichiometric $BaCa(CO_3)_2$ samples did not exceed 75% of the theoretical density, whereas with $BaCO_3$ additive the densification reached about 90%. The effect of the heat treatment time is shown in Fig. 5. Once again, $BaCO_3$ additive allowed dense pellets to be obtained more quickly. After only 2 h of treatment the pellets already reached about 80% of the theoretical density. With stoichiometric materials, however, 2 h of treatment were not sufficient to densify the material: the d/d_{theo} ratio was nearly the same before (52%) and after heat treatment (54%). After 2 h of heat treatment at

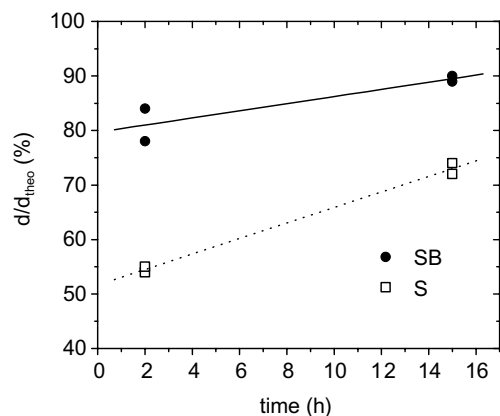


Fig. 5. Effect of heat treatment time on sample densification. Temperature: 580 °C.

580 °C, SEM microstructural examination of an ‘S’ sample compared with an ‘SB’ sample (see Fig. 6), clearly shows the densification of the ‘SB’ material, while the ‘S’ material is only an agglomeration of powder grains.

- **Hardness:** There were no major differences among the samples. In every case the measured Vickers hardness was about 4 (Mohs scale).

As mentioned above, excess BaCO_3 is necessary to obtain a non-friable densified pellet of mixed carbonate $\text{BaCa}(\text{CO}_3)_2$ by natural sintering. Although densification occurs with stoichiometric concentrations, it does not exceed 75% of the theoretical density and the pellets are friable.

Sintering additives are used for other types of ceramics [10], as well as for calcium carbonate [8]. For borides or carbides that are very difficult to sinter, adding an

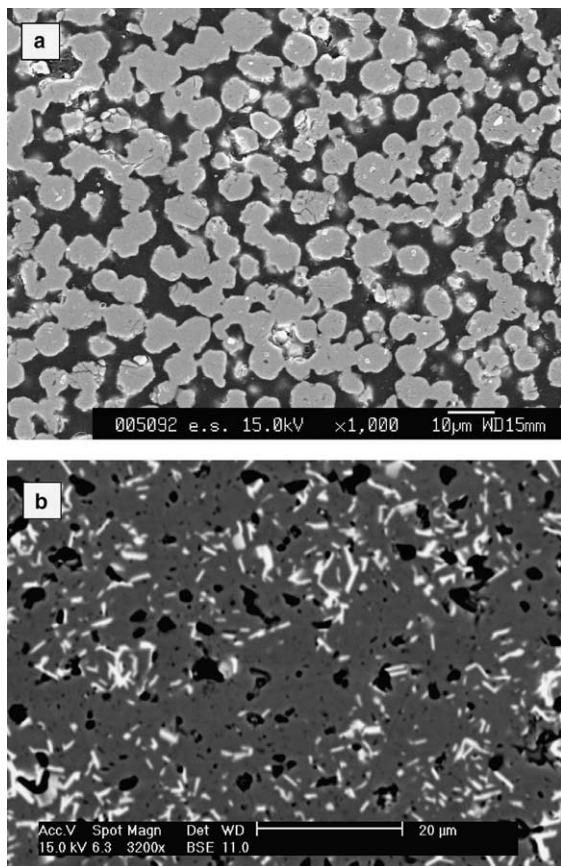


Fig. 6. Microstructural observations. (a) $\text{BaCa}(\text{CO}_3)_2$ pelletized at 15 MPa and sintered for 2 h at 580 °C; the ‘black’ phase is the encapsulation resin, the white phase corresponds to $\text{BaCa}(\text{CO}_3)_2$ and (b) $\text{BaCa}(\text{CO}_3)_2 + \text{BaCO}_3$ (SB0.2) pelletized at 15 MPa and sintered for 2 h at 580 °C; the white phase is enriched in Ba compared with the grey phase.

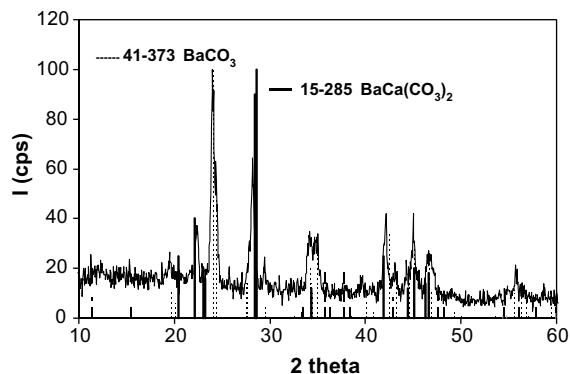


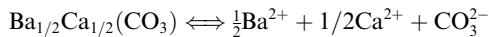
Fig. 7. Diffraction diagram of a powder mixture: 4 g $\text{CaCO}_3 + 16$ g BaCO_3 after 2 h at 580 °C.

impurity such as Mo, Cr or Ni can facilitate sintering by forming a secondary phase during sintering [10]. These considerations suggest that the improved sintering behavior of the $\text{BaCa}(\text{CO}_3)_2$ – BaCO_3 mixture could be due to a solid-state reaction between barium carbonate and the mixed Ba–Ca carbonate. This reaction could enhance the cohesion among the powder grains, ensuring greater hardness and better densification. As shown in Fig. 1(b) the comparison of the X-ray diffraction diagrams of a mixture SB0.2 before and after shrinkage show the absence of secondary phases or decomposition products. Moreover, the peak intensity of BaCO_3 is lower after sintering than before, which could be attributed to a reaction between these two carbonates during the sintering heat treatment. The CaCO_3 – BaCO_3 phase diagram [5,11] includes a large $\text{BaCa}(\text{CO}_3)_2$ stability range. For example, it can accept up to 9 mol% excess BaCO_3 at 750 °C without losing the monoclinic properties of barytocalcite. We tested a mixture of 4 g of pure CaCO_3 with 16 g of pure BaCO_3 , submitted to heat treatment for 2 h at 580 °C. The diffraction diagram for this powder reveals a partial reaction between the two carbonates, as indicated by the presence of $\text{BaCa}(\text{CO}_3)_2$ (see Fig. 7). The two carbonates can thus react during the sintering heat treatment. The hypothesis of a reaction between excess BaCO_3 and $\text{BaCa}(\text{CO}_3)_2$ during sintering appears plausible, and could account for the fact that in this case the pellets densification was greater with excess BaCO_3 .

3.3. Aqueous alteration

An alterability test was carried out in static mode to determine the solubility product at 90 °C of a 90% densified ‘SB0.2’ $\text{BaCa}(\text{CO}_3)_2$ pellet. A Savillex leaching cell containing the test pellet in pure water was placed in a controlled temperature chamber at 90 °C. ICP-AES analysis of a water sample taken after 7 days indicated

a Ba^{2+} concentration of 0.66 mg/L. This corresponds to a $\text{p}K_s$ value of 10.6 for the following reaction:



An alterability test was carried out in dynamic mode to determine the solubility product of an 84% densified ‘SB0.2’ $\text{BaCa}(\text{CO}_3)_2$ pellet. The test was carried out at 100 °C, with pure water continuously evaporated in a 300 cm³ boiler, condensed in a cooler, allowed to flow into the sample boat and overflow into the boiler again. This system ensured a constant flow of pure water onto the sample, while concentrating the leached elements in the boiler. This test procedure is extremely unfavorable in the case of carbonates, where the alterability is determined by the solubility product, and is poorly representative of geological disposal conditions, since the water is continuously renewed. Nevertheless, with our sample the Ba^{2+} and Ca^{2+} concentrations in solution in the boiler increased during the first day of the test (Fig. 8): the alteration rate (slope) was about 924 g m⁻² d⁻¹. The greater solubility of Ba is attributable to the excess of BaCO_3 in the pellet. Beyond 1 day, the Ba and Ca concentrations remained almost constant which indicate that the carbonate solubility limit was largely reached in the boiler. The plateau observed after 1 day thus represents an equilibrium between Ca and Ba precipitation in the boiler and dissolution of the carbonate by the flow of pure water. Then the residual rate observed represents directly this pure water flow. Indeed, after testing, the Ba and Ca precipitates were redissolved when the boiler was acidified.

These findings clearly demonstrate that if geological disposal is considered for this type of matrix, it must be situated in a limestone formation. Under these conditions, the groundwater coming into contact with the package would be saturated in CO_3^{2-} (and Ca^{2+}) ions because of the calcareous environment, thereby minimizing aqueous alteration of the carbonate pellets.

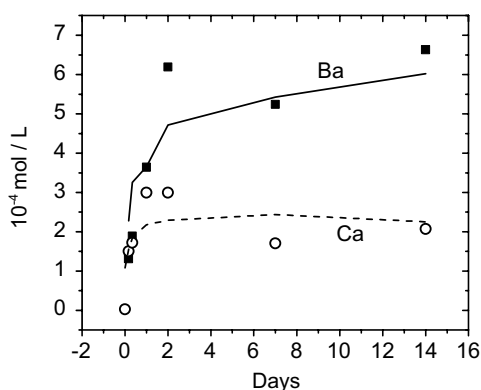


Fig. 8. Results of dynamic alteration test at 100 °C.

Nevertheless, the possible effect of isotopic exchange between ¹²C in calcareous groundwater and ¹⁴C in the carbonate waste package must be assessed by additional leach tests using water saturated with CO_3^{2-} .

4. Conclusion

We have shown that natural densification is possible in the case of a mixed carbonate, $\text{BaCa}(\text{CO}_3)_2$. Excess BaCO_3 is necessary to obtain pellets with a bulk density exceeding 80% of the theoretical density and to ensure sufficient material hardness. We attribute this result to a solid-state reaction occurring between BaCO_3 and $\text{BaCa}(\text{CO}_3)_2$ during the sintering heat treatment, resulting in enhanced material densification.

Press compaction at 150 MPa followed by natural sintering for 15 h at 580 °C of alstonite powder with superstoichiometric BaCO_3 yields pellets with the following properties:

- densification exceeding 80%,
- high hardness (about 4 on the Mohs scale),
- approximately 8 wt% carbon content for a density of 3.7 g cm⁻³, corresponding to a waste volume of 3.3 dm³ to immobilize 1 kg of carbon (see Table 1).

A $\text{p}K_s$ value of -10.6 for the $\text{Ba}_{1/2}\text{Ca}_{1/2}(\text{CO}_3) \rightleftharpoons \frac{1}{2}\text{Ba}^{2+} + \frac{1}{2}\text{Ca}^{2+} + \text{CO}_3^{2-}$ reaction was measured in the laboratory. The chemical durability was assessed using a high temperature test (100 °C) in initially pure water. During the first day of the test, the dissolution rate measured was high (~924 g m⁻² d⁻¹). Nevertheless beyond 1 day, the Ba and Ca concentrations remained constant thus indicating the chemical stability of such ceramic under carbonate saturated aqueous solutions.

References

- [1] R.D. Scheele, L.L. Burger, Selection of a carbon 14 fixation form, 1982, PNL 4447 DE83003319.
- [2] A.G. Croff, An evaluation of options relative to the fixation and disposal of ¹⁴C-contaminated CO_2 as CaCO_3 , ORNL TM-5171, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
- [3] I.H. Brooks, C.A. Heath, B. Kirstein, D.G. Roberts, Carbon-14 in the HTGR Fuel Cycle, General Atomic Company, San Diego, California, 1974.
- [4] A. Grandjean, G. Leturcq, C. Baron, Utilisation de carbonates mixtes frittés pour le confinement de carbone radioactif, Patent EN 03/12591.
- [5] L.L.Y. Chang, Amer. Mineral. 56 (1971) 1660.
- [6] N. Yamasaki, W. Tang, J. Ke, J. Mater. Sci. Lett. 11 (1992) 934.
- [7] N. Yamasaki, W. Tang, J. Ke, K. Hosoi, J. Mater. Sci. Lett. 14 (1995) 1268.

- [8] Ishida Hideki, Method for sintering calcium carbonate under atmospheric pressure, Patent JP7242415 (1995-09-19).
- [9] F. Takao, Method for sintering alkaline earth carbonate compound, Patent JP6080476 (1994-03-22).
- [10] T. Ide, K. Nakano, T. Ando, Powder Metall. Int. 20 (1988) 21.
- [11] W.R. Brice, L.L.Y. Chang, Amer. Mineral. 58 (1973) 979.