

## BEHAVIOR OF COMMON ROCK-FORMING MINERALS IN A STRONGLY BASIC NaOH SOLUTION

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### ABSTRACT

The pH of the pore solution existing within concretes or lime-treated soils normally exceeds 12. When exposed to a solution with a pH over 10, several rock-forming and soil-forming minerals are unstable, and dissolve with or without precipitation, depending on the nature and concentration of species in solution. In concrete, made with a typical cement containing 0.7% to 1% alkalis, after a few days, the composition of the liquid phase is dominated by sodium, potassium and hydroxide ions. In this study, the behavior of several common minerals in a pure sodium hydroxide solution was evaluated by the means of two experiments. First, mineral fragments were immersed in a 1N NaOH solution at 23°C for 265 days, then at 80°C for 7 days. The specimens were regularly analyzed with a SEM-EDX system. Secondly, the release of silica by silicate minerals in a 1N NaOH solution was measured by means of the Chemical Method ASTM C 289 test (80°C, 24 hours). Of all the silicate minerals tested, the microcrystalline variety of silica, chert, was the most unstable phase. Significant quantities of silica also were released by quartz and feldspars. Iron and magnesium silicates were found to be the most stable phases in the NaOH solution. Among the other minerals investigated, dolomite, siderite and gypsum are classified as highly reactive in the alkaline solution.

**Keywords:** rock-forming minerals, soil-forming minerals, concrete aggregates, sodium hydroxide, chemical stability, ASTM C 289, scanning electron microscopy.

### SOMMAIRE

Le pH de la solution interstitielle au sein du béton ou d'un sol stabilisé à la chaux est normalement supérieur à 12. Plusieurs minéraux communs des roches et des sols sont instables dans un milieu à pH supérieur à 10. Ils sont généralement dissouts et, selon la nature et la concentration des espèces en solution, des précipités pourront se former. Dans le béton, fabriqué à partir d'un ciment normal contenant de 0.7% à 1% d'alkalis, après seulement quelques jours, la solution interstitielle est dominée par les ions sodium, potassium et hydroxydes. Dans cette étude, une évaluation du comportement de plusieurs minéraux communs dans une solution d'hydroxyde de sodium a été entreprise à l'aide de deux séries d'essais. Dans un premier temps, des fragments de minéraux ont été immergés dans une solution de 1N NaOH à 23°C pendant 265 jours, puis à 80°C pendant 7 jours. Les échantillons ont été régulièrement examinés en cours d'essai au microscope électronique à balayage. Dans un deuxième temps, la libération de silice par les silicates, toujours dans une solution de 1N NaOH, a été mesu-

rée par l'essai standard de la Méthode Chimique ASTM C 289 (80°C, 24 heures). De tous les silicates évalués, le chert, variété microcristalline de silice, a été classifié comme étant le matériau le plus instable. Des quantités non négligeables de silice ont aussi été libérées par le quartz et les feldspaths. Les silicates de fer et de magnésium se sont révélés relativement stables dans une telle solution. Parmi les autres minéraux étudiés, la dolomite, la sidérite et le gypse ont été reconnus comme très réactifs en solution alcaline.

**Mots-clés:** minéraux des roches, minéraux des sols, granulats à béton, hydroxyde de sodium, stabilité chimique, ASTM C 289, microscopie électronique à balayage.

### INTRODUCTION

In nature, the common minerals in soils and rocks are generally in contact with water at a pH between 4 and 8. In extreme cases, the pH can be as low as 2, in the presence of sulfides, which oxidize to give H<sub>2</sub>SO<sub>4</sub> (Bérubé *et al.* 1986), and as high as 10, in the presence of alkaline salts such as Na<sub>2</sub>CO<sub>3</sub> (Bruckert & Rouiller 1979). In an artificial material such as concrete, aggregate minerals are submitted to a concentration of OH<sup>-</sup> that can exceed 0.7 mole/litre, which corresponds to a pH higher than 13.5 (Longuet *et al.* 1973, Bérubé *et al.* 1988). Also, where the pore water of a soil is saturated with lime, as in the case of lime stabilization, pH values of 12.4 are measured (Choquette *et al.* 1987, Bérubé *et al.* 1988). In the first example, what is known as "alkali-aggregate reactions" can develop and cause concrete expansion and microcracking (Bérubé *et al.* 1988, Bérubé & Fournier 1986). In the second example, solubilization of silicates will lead to the formation of cementing hydrated calcium silicates (CSH) that will improve soil strength. The main goal of this research was to improve our knowledge on the behavior and the reactivity of several common minerals in a high-pH alkaline solution. More precisely, the degradation of several minerals in a sodium hydroxide solution has been studied. Also, the relative reactivity of silicate minerals has been established according to the amount of silica released during the ASTM Chemical Method C 289, which was originally designed to evaluate the reactivity potential of silicate aggregates in concrete. This study of the behavior of pure mineral species in a high-pH solution will help in the interpretation of numer-

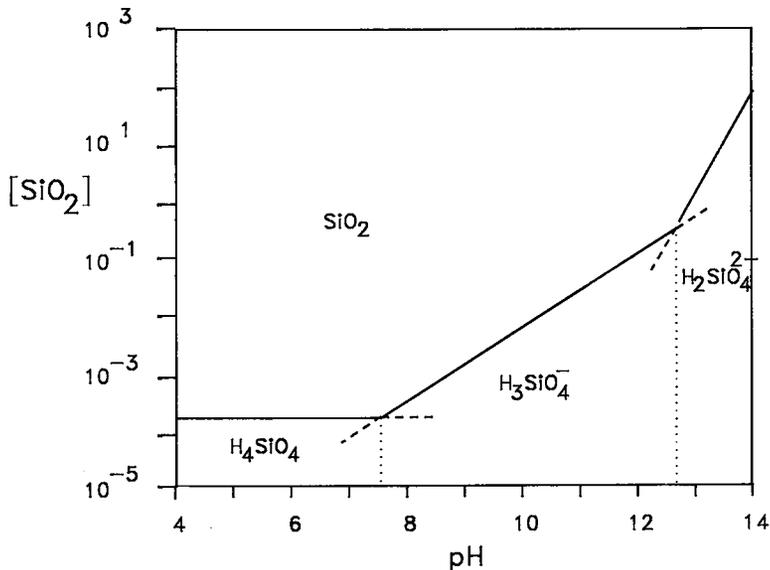


FIG. 1. Theoretical solubility of quartz with respect to pH. Curves calculated from data of Stumm & Morgan (1981).

TABLE 1. MINERALS TESTED

Mineral	Mineral fragment in an epoxy resin mount	ASTM C 289 Chemical Method
<b>Silica minerals</b>		
Quartz	X	X
Chert	X	X
<b>Feldspars</b>		
Microcline	X	X
Oligoclase	X	X
Labradorite	X	X
<b>Amphiboles and pyroxenes</b>		
Hornblende		X
Actinolite	X	X
Augite	X	X
Diopside	X	X
<b>Clay minerals and other Mg-silicates</b>		
Biotite	X	X
Metabentonite (API #42)		X
Chlorite	X	X
Serpentine		X
Olivine		X
<b>Carbonates</b>		
Calcite	X	X
Dolomite	X	X
Siderite		X
<b>Other minerals</b>		
Gypsum		X
Goethite		X
Nepheline		X

ous observations related to soil-lime stabilization and alkali-aggregate reactions in concrete.

### Chemical considerations

In a solution with a pH higher than 7.5, silica solu-

bility increases dramatically (Iler 1979). The concentration and the nature of the dominant species of silica in solution depend upon pH (Fig. 1). At pH under 7.5, the solubility of quartz is low ( $10^{-3.7}$  M). The main silica species in solution is the neutral orthosilicic acid ( $H_4SiO_4$ ). Between pH 7.5 and approximately 12.5, the solubility of quartz increases to about  $10^{-1}$  M, and ionized silicic acid becomes the dominant species. At a pH higher than 12.5, the solubility of quartz increases further with pH,  $H_2SiO_4^{2-}$  being the dominant species. The solubilization of silica in an alkaline solution is considered to proceed in several steps (Dent Glasser & Kataoka 1981). First, the surficial acid silanol groups are attacked by the hydroxyl ions, producing (Si-O)<sup>-</sup> groups which, in turn, are counterbalanced by alkali ions. The siloxane bridges then are attacked, again by the OH<sup>-</sup> ions, producing more (Si-O)<sup>-</sup> groups, releasing silica ( $H_2SiO_4^{2-}$  at pH 13.5). The silica-bearing mineral species that are poorly ordered, hydrated or porous, are more sensitive and will react faster than the well-ordered crystalline forms (Diamond 1976). The solubility products of quartz and amorphous silica reflect this state (quartz:  $K_{sp} = 10^{-3.7}$ , amorphous silica:  $K_{sp} = 10^{-2.7}$ ).

In a dilute solution of NaOH, silica gel dissolves until equilibrium with the solution is reached, without any precipitation (Dent Glasser & Kataoka 1982). If calcium is introduced in the solution, a hydrated calcium silicate will precipitate (CSH gel). Precipitation of such a phase is possible even if a minute amount of calcium is present in solution, since its solubility product is very low (CSH gel:  $K_{sp}$

TABLE 2. CHEMICAL COMPOSITION OF TESTED MINERALS (EXPERIMENT ON FRAGMENTS)

	Qtz	Bt	Dol	Cal	Olg	Lab	Mc	Chert	Chl	Aug	Act	Di
SiO <sub>2</sub>	98.00	36.70	1.10	0.40	62.00	48.60	64.30	87.60	31.10	48.60	53.60	54.50
Al <sub>2</sub> O <sub>3</sub>	0.35	20.50	0.51	0.50	22.70	30.00	17.90	0.94	35.20	2.87	1.48	2.59
FeO <sub>t</sub>	1.42	24.60	2.75	0.05	0.12	6.37	0.05	0.58	8.05	15.84	6.63	6.50
MnO	0.01	0.35	0.12	0.05	0.02	0.01	0.01	0.01	0.09	0.74	0.20	0.30
MgO	0.24	6.77	20.00	0.47	0.18	0.18	0.10	0.68	19.20	8.51	13.90	19.20
CaO	0.55	0.20	29.50	56.80	4.45	9.45	0.34	5.27	0.30	19.50	22.00	12.60
Ni <sub>2</sub> O	0.07	0.27	0.05	0.06	8.26	4.72	2.60	0.15	0.15	1.19	0.33	0.57
K <sub>2</sub> O	0.04	8.42	0.07	0.01	0.85	0.40	11.90	0.10	1.86	0.19	0.10	0.07
CO <sub>2</sub>	---	---	45.60	43.20	---	---	---	---	---	---	---	---
LOI	---	---	---	---	1.33	0.80	0.13	4.07	---	0.50	0.15	1.47
TOTAL	98.68	97.81	99.70	101.54	99.91	100.53	97.33	99.40	95.95	97.94	98.39	97.80

All values in weight %. ---: not available Method of analysis: AAS  
 1: Low TOT value is due to missing LOI.

= 10<sup>-9</sup> for C:S = 1:1, Gartner & Jennings 1987). Alumina behaves in a very similar way. In a NaOH solution, it dissolves until equilibrium is reached in the solution. Again, if calcium is introduced, a hydrated calcium aluminate (CAH) is likely to precipitate. In these two cases, precipitation of CSH and CAH consume OH<sup>-</sup> ions, which decreases the pH accordingly. Hydrated calcium aluminosilicates are possible reaction products where both silica and alumina coexist with calcium in the high-pH solution. The exact chemical composition of these hydrated phases is a function of many factors, such as the concentration of their constituents in the solution, temperature and pH.

Reaction mechanisms between silicate minerals and alkaline solutions are not well understood, even if it is well established that several silicates, in particular silica-rich clay minerals, are capable of producing hydrated cementing phases in a calcium hydroxide solution (Bérubé *et al.* 1990, Choquette 1988, Van Aardt & Visser 1977, 1978, Glenn & Handy 1963, Diamond *et al.* 1964, Le Roux 1969). Less ordered and charge-deficient layered mineral phases like montmorillonite are more sensitive to a high-pH environment (Carroll & Starkey 1971, Ferrell & Grim 1967). Carbonates, and in particular dolomite, can react in such solutions. Dolomite is already known to be unstable in the high-pH pore solution in concrete; it breaks down to CaCO<sub>3</sub> (calcite) and Mg(OH)<sub>2</sub> (brucite) (Hadley 1961, Gillott 1964, Poole & Sotiropoulos 1980). This reaction also has been observed in cases where dolomite is placed in contact with a saturated lime solution (Bérubé *et al.* 1990). To our knowledge, the behavior in high-pH solutions of amphiboles and pyroxenes, abundant in many rocks, has never been studied.

#### EXPERIMENTAL PROCEDURE

In a first experiment, a small fragment of mineral approximately 5 mm in diameter (total surface of less than 25 mm<sup>2</sup>) was fixed to a cylindrical mount made of epoxy resin, with only one natural broken

surface (irregular or a cleavage plane) exposed. Table 1 lists the minerals tested in this experiment. Their chemical composition is given in Table 2. The resin mount supporting the mineral was then immersed in 100 mL of a 1N NaOH solution inside a hermetically sealed polyethylene bottle. Periodically (after 1, 14, 28, 84 and 265 days), each mount was removed from solution and thoroughly but gently washed with distilled water to eliminate any NaOH that could precipitate as sodium carbonate by reaction with air. For SEM observations, the sample was dried for 24 hours at 50°C, and coated with aluminum. This coating can be easily removed after SEM examination, by immersing the sample in another sodium hydroxide solution. The mount was then returned in its original NaOH solution. This method allowed periodic examination of the same region of interest on the mineral surface, thus supplying information on the progress of chemical reactions. After 265 days, the temperature of the solution was raised to 80°C for another 8 days, to accelerate the process.

In a second experiment, mineral samples were subjected to the Chemical Method ASTM C 289 test, in which 25 g of material of size 300 to 150 µm is allowed to react with 25 mL of a 1N NaOH solution at 80°C for 24 hours. Silica in solution and reduction in alkalinity (acid titration) are then measured. In addition to the 12 minerals tested in the first experiment, eight others were added (Table 1). Although several of them are not silicates, they were tested in order to measure reduction in alkalinity and to examine newly formed solids.

#### RESULTS AND DISCUSSION

##### *Experiment on mineral fragments*

After 265 days in a NaOH 1N solution at 23°C, SEM observations revealed that only two minerals reacted significantly: calcite and dolomite. All other minerals appeared unattached, no sign of dissolution or precipitation being detected. After only 28 days, the calcite crystal was strongly corroded,

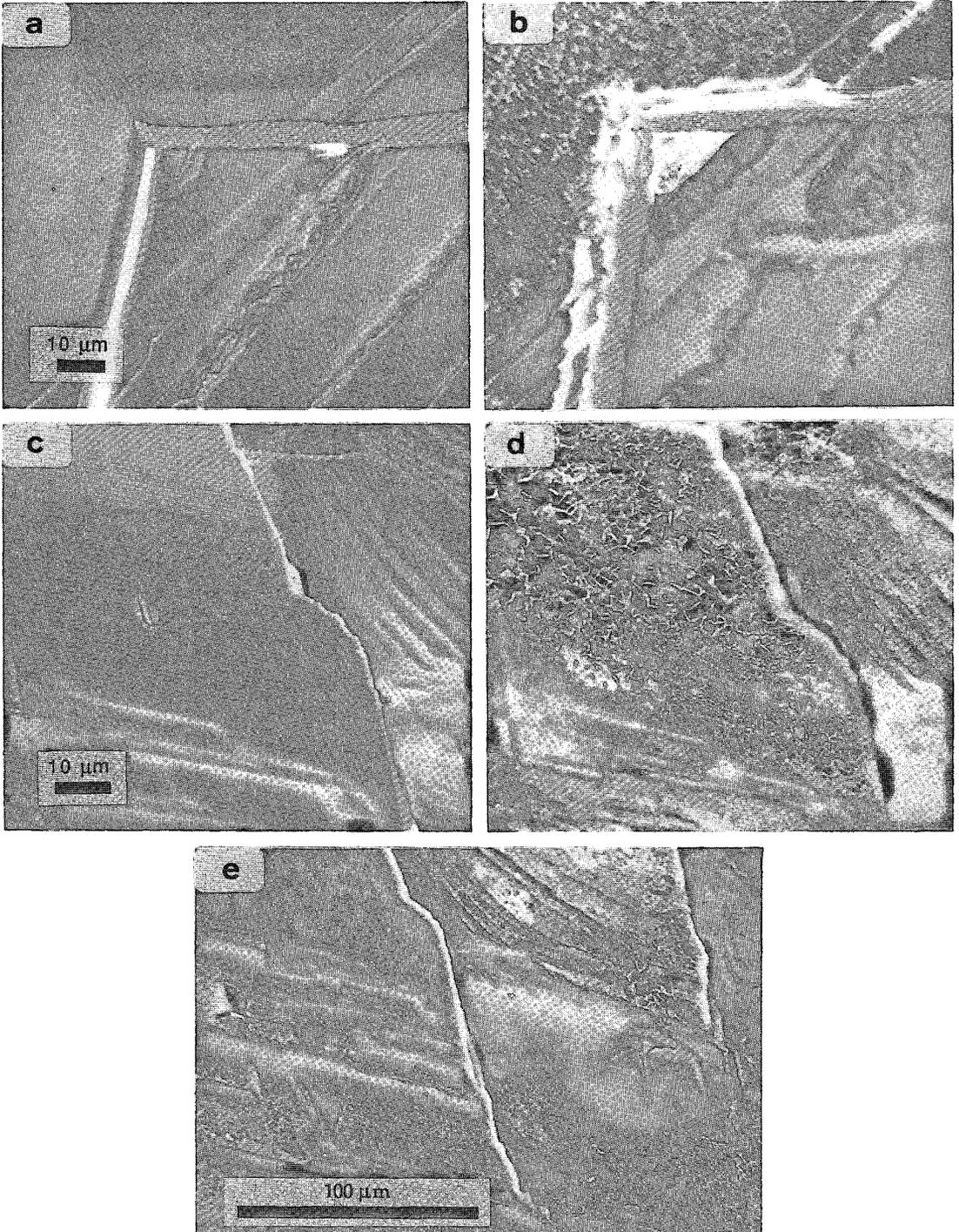


FIG. 2. SEM photomicrographs of the calcite and dolomite fragments. a and b: Original surface of calcite and its appearance after 28 days in the 1N NaOH solution at 23°C. c and d: Original surface of dolomite and its appearance after 28 days in the 1N NaOH solution at 23°C. Brucite flakes are clearly visible. e: "Pop up" feature on dolomite after 60 days of contact with the alkaline solution.

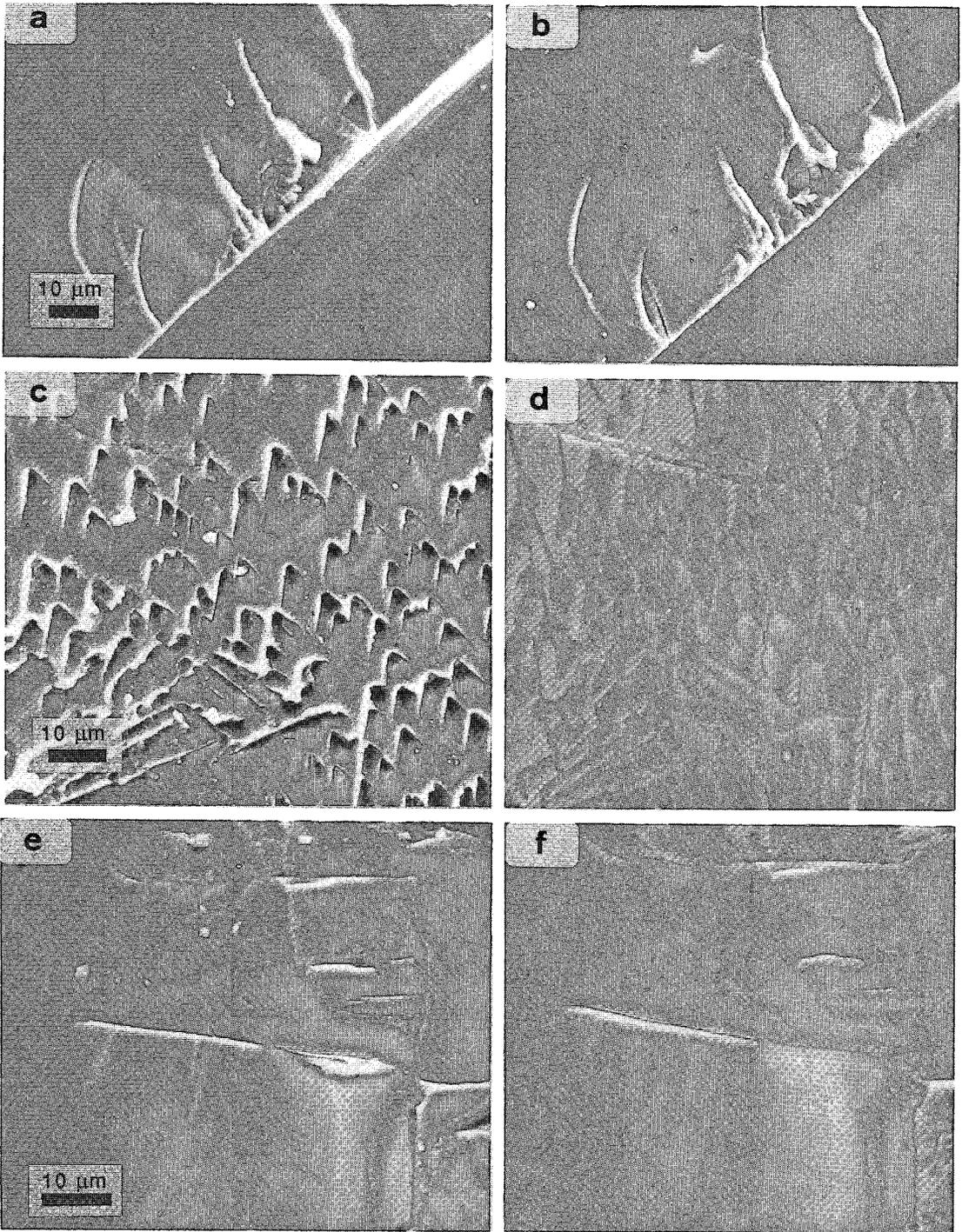


FIG. 3. SEM photomicrographs of quartz and feldspars fragments after 7 days at 80°C in the 1N NaOH solution. a and b: Quartz. Surface dissolution in b is not oriented. c: Original surface of labradorite. d: Oriented dissolution pattern on labradorite. e: Original surface of oligoclase. f: Dissolution occurring along preferred orientations or defects in oligoclase.

without precipitation. Dissolution is preferentially oriented along cleavage and twin planes (Figs. 2a, b). Between 28 and 256 days, no significant change was observed, which suggests that dissolution and equilibrium with the solution took place early. Dolomite also reacted strongly with the alkaline solution within 28 days of immersion. Brucite was clearly identified as a product of the dedolomitization reaction; it covers the surface of the crystal (Figs. 2c, d). Calcite, the other product expected in this reaction, was not detected. Since a small quantity of calcite can be dissolved in the NaOH solution, as observed for the calcite crystal, no calcite can form until the solution becomes saturated. Indeed, calcite crystals were observed after the sample was transferred at 80°C for 7 days; oversaturation with respect to this mineral was reached within this time. After 60 days at 23°C, "pop up" features appeared (Fig. 2e). These probably result from volume increase inside the surface layer of brucite with respect to dolomite and represent local release of stresses. Such a mechanism was suggested by Carles-Gibergues *et al.* (1989) to partly explain the expansion of concrete containing a dolomitic limestone aggregate, as a result of alkali-carbonate reactions.

Surprisingly, all silicate minerals, including chert and quartz, showed no evidence of reaction after 265 days of immersion in the alkaline solution at 23°C, despite the fact that quartz, for example, reacts with a lime solution at room temperature to produce CSH (Bérubé *et al.* 1990). We contend that the release of silica by silicate minerals, normally more important in a 1N NaOH solution (pH = 14) than in a saturated lime solution (pH = 12.4), was not sufficiently important to be perceived by means of SEM obser-

vations, according to the experimental conditions used for the test. That is why we decided to subject the samples to a temperature of 80°C for a supplementary curing period of 7 days, after the first 265 days at 23°C, in order to accelerate the reactions.

Following the hot NaOH treatment, evidence of corrosion became apparent on quartz, oligoclase, labradorite and microcline. Biotite and chert also reacted with the hot sodium hydroxide solution. Chert was dissolved to such an extent that the original area of interest could not be found. Actinolite, augite, diopside and chlorite stayed unchanged after this aggressive treatment. In general, dissolution of quartz and the feldspars can be qualified as light. With quartz, dissolution proceeded as randomly oriented etch pits (Figs. 3a, b). With labradorite and oligoclase, dissolution occurred along preferential orientations (Figs. 3c, d, e, f). The exposed surface of microcline shows signs of a slight dissolution, without specific orientation.

With all the silicate minerals, there was no evidence of newly formed phases. It was expected, at least for the calcic plagioclase, that the release of calcium and silica in the solution would trigger a precipitation of a CSH. This did not happen, perhaps because of the very large volume of solution (50 mL) compared to the minute volume of dissolved mineral. The concentrations of calcium and silica in solution probably never reached values high enough to exceed saturation with respect to CSH. Since the solubility mechanisms of the CSHs are very complex and still under study, we will not speculate further on this point. All the feldspars tested dissolved in quite similar amounts, suggesting a common level of reactivity of this group of minerals.

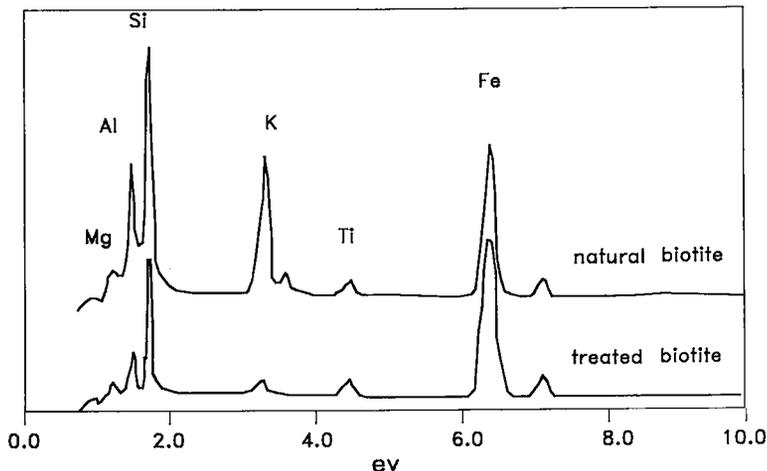


FIG. 4. Energy-dispersion X-ray spectrum of natural biotite and after the NaOH treatment. Note the near-complete loss of K and relative increase in Fe in the treated sample.

Biotite also reacted with the hot NaOH solution, its surface becoming completely blistered, with many layers dissolved. EDX analyses before and after the treatment revealed a near-complete loss of potassium and significant removal of silicon and aluminum compared to iron (Fig. 4). This observation strongly suggests a reaction mechanism that allows the removal of interlayer K followed by exposure and dissolution of the sheets of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra, which leaves an amorphous coating of iron hydroxide. This mechanism could also explain why the Mg-chlorite did not react with the NaOH solution: the interlayer space is occupied by a stable brucite-type layer of octahedra, which does not allow infiltration of the solution and dissolution of the layers of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra. The same explanation may apply to the other Fe-Mg silicates tested (amphiboles and pyroxenes). It is possible that, as the surface Si- and Al-bearing tetrahedra are dissolved by the alkaline solution, a protective layer of residual iron or magnesium hydroxide builds up, which thus reduces or completely prevents further dissolution. More research is needed to verify these hypotheses.

#### Chemical Method ASTM C 289

In the second experiment, as mentioned above, several other minerals were tested. Results for the silicate minerals will be presented first, followed by the observations made on the other minerals.

Values of silica released ( $Sc$ ) by the silicate minerals in a 1N NaOH solution (80°C, 24 hours), according to the Chemical Method ASTM C 289, are presented in Table 3, along with the reduction  $Rc$  in alkalinity of the solution (acid titration down to the phenolphthalein point). The significance of  $Rc$  will not be discussed in detail but does serve in some cases to explain the behavior of the non-silicate minerals. Table 3 shows, that chert clearly departs from the other minerals, as its  $Sc$  value is 183 mmoles/L. Such a high value was expected from the results described above. Next, biotite, quartz and metabentonite have the highest  $Sc$  values, 18, 17 and 13 mmoles/L, respectively. The feldspars define a coherent group, with  $Sc$  values between 7 and 9 mmoles/L. As in the case of the first experiment on mineral fragments, there is no significant difference among these minerals. Under the SEM, there is no evidence of preferentially oriented patterns of dissolution, as observed before, probably because of the shorter time in the NaOH solution. For the remaining silicates,  $Sc$  values below 6 mmoles/L were measured, and no sign of corrosion was detected (SEM observations).

In order to quantify the capacity of a silicate mineral to release its silica content in the NaOH solution, the measured values of dissolved silica have

TABLE 3. SUMMARY DATA FOR THE ASTM C 289 CHEMICAL METHOD

Mineral	SiO <sub>2</sub> (%)	Sc <sup>1</sup> (mmoles/l)	Rc <sup>2</sup> (mmoles/l)	Sc/%SiO <sub>2</sub>
Chert	87.6	183	68	2.09
Biotite	36.7	18	0	0.49
Metabentonite	54.0*	13	255	0.24
Quartz	96.0	17	11	0.18
Oligoclase	62.0	9	4	0.15
Labradorite	48.6	7	0	0.14
Microcline	64.3	8	6	0.12
Augite	48.6	6	7	0.12
Chlorite	31.1	3	2	0.10
Serpentine	42.0*	4	43	0.10
Olivine	35.0*	3	0	0.09
Nepheline	42.3*	3	8	0.07
Hornblende	43.0*	3	32	0.07
Diopside	54.5	3	20	0.06
Actinolite	53.6	2	13	0.04
Calcite		2	5	
Dolomite		1	275	
Siderite		3	457	
Gypsum		1	837	
Goethite		5	327	

\* Estimated value. 1.  $Sc$  = Concentration of  $\text{SiO}_2$  in the 1N NaOH solution. 2.  $Rc$  = Reduction in alkalinity of the solution measured by acid titration down to the phenolphthalein point compared to a pure NaOH 1N solution.

been plotted against the silica content of each mineral. In such an approach, it is assumed that all the dissolved silica remains in solution, without interaction with other species, in particular calcium. This approach is validated by the fact that in most cases, newly formed silica-bearing hydrates have not been observed. Results are given in Figure 5 and Table 3. Chert is by far the most reactive mineral, with a  $Sc/\%SiO_2$  ratio of more than 2. This phase is known to cause some problems in concrete (Dolar-Mantuani 1983). Because of its microcrystalline nature in chert, silica is rapidly dissolved in the highly basic and alkaline pore solution present in concrete and reacts with  $\text{Ca}^{2+}$  ions [or with solid portlandite  $\text{Ca}(\text{OH})_2$ ] to precipitate as expansive CSH gels. Well-crystallized and unstressed quartz is, on the other hand, generally innocuous in concrete. It released 0.18 mmoles/L of silica per unit of  $\text{SiO}_2$  content, which is ten times less than chert. Feldspars, with a lower corresponding ratio, between 0.10 and 0.15, also are considered innocuous in concrete. The second most reactive silicate tested is biotite, with a normalized ratio of dissolved silica just below 0.5. This confirms the qualitative observations made in the first experiment. The reactivity of biotite is attributed to the capacity of the alkaline solution to penetrate the interlayer space, to remove potassium and to expose the layer of  $\text{SiO}_4$  tetrahedra. Results on metabentonite are a little confusing. Its microcrystalline nature led us to expect it to be more

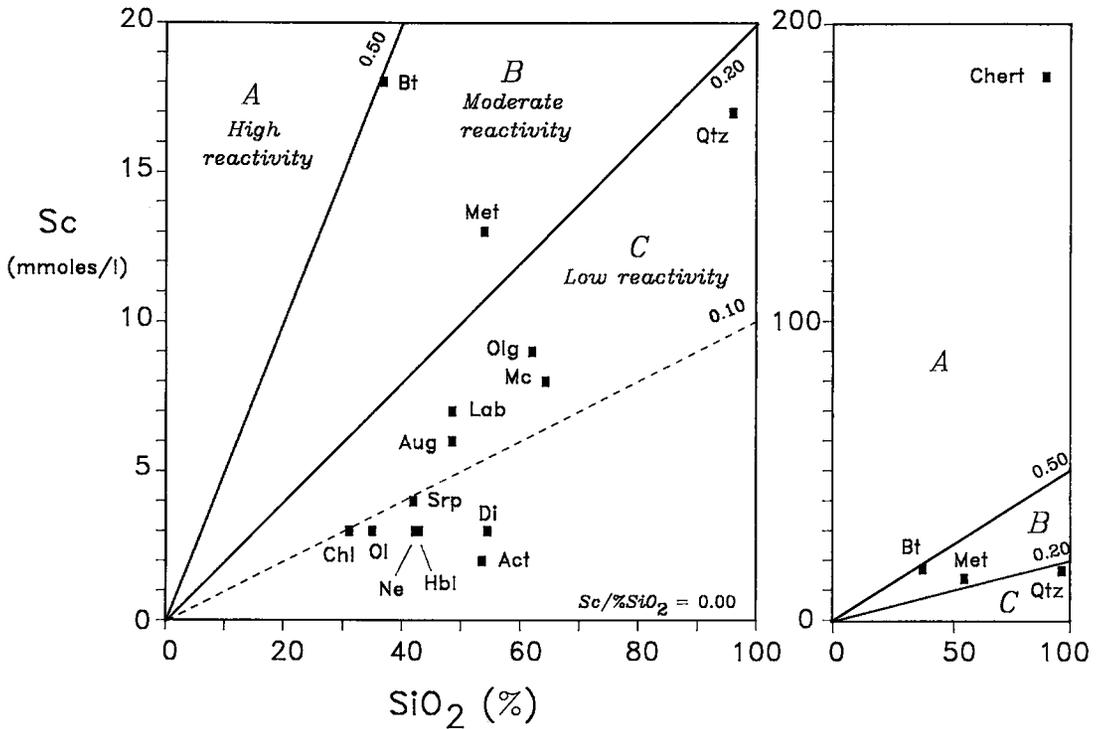


FIG 5. Silica in solution at the Chemical Method ASTM C 289 ( $Sc$ ) versus silica content of silicate minerals ( $\% SiO_2$ ). Areas of A: High reactivity, B: Moderate reactivity and C: Low reactivity are shown.

reactive than quartz, but its normalized silica ratio is 0.24, almost equal to the value for quartz. This behavior is probably related to some other interaction in solution, since an important reduction in alkalinity of 255 mmoles/L was measured. However, no silica-bearing hydrate was observed under the SEM. Minerals like biotite and metabentonite could be problematic in concrete if they are abundant in the aggregate. However, this is rarely the case because of consequent undesirable mechanical properties. All the other Fe-Mg silicates show normalized ratios of dissolved silica below 0.12, which confirms their relative stability in the alkaline solution. Results on nepheline provide another area of confusion at present. Though it releases only 3 mmoles/L of silica to the solution, signs of corrosion were detected through SEM observations (Fig. 6a). Nepheline has already been found to be reactive in presence of lime, producing CASH-type hydrates (Bérubé *et al.* 1990). In the present case, the reduction of alkalinity was minimal (8 mmoles/L). Further research definitely is needed on this mineral, since nepheline-rich rocks (syenites or phonolites) often are used in concrete, apparently without problem (Ouellet 1988).

According to the preceding discussion, limiting values of the  $Sc/\%SiO_2$  ratio can be tentatively

drawn between reactive, slightly reactive and unreactive silicate minerals in basic and alkaline solutions. All minerals tested with a ratio under 0.20 are known to be innocuous in concrete. Chert, with a ratio over 2.00, is highly reactive. Since serious doubts can arise about the chemical performance of the two minerals with ratios between 0.20 and 0.50 (biotite and metabentonite), these limits are suggested for the moderately reactive minerals. The significance of these limits depends on the specific applications. Up to now, the release of silica has been used to evaluate the chemical performance of minerals in concrete. For soil-lime stabilization, the mechanisms are essentially similar (Bérubé *et al.* 1988), and these values can be used to evaluate the potential of silicate minerals to produce cementing hydrates. For example, in the context of another study related to the evaluation of mineral reactivity in the presence of  $Ca(OH)_2$  (Bérubé *et al.* 1990), the proposed classification of reactivity is in good agreement with the results given here. In soil-lime stabilization, a slight production of calcium hydrate may lead to large improvements of mechanical performance of a treated soil (Choquette 1988). Thus the contribution of marginally reactive minerals, like the feldspars, cannot be neglected under favorable conditions

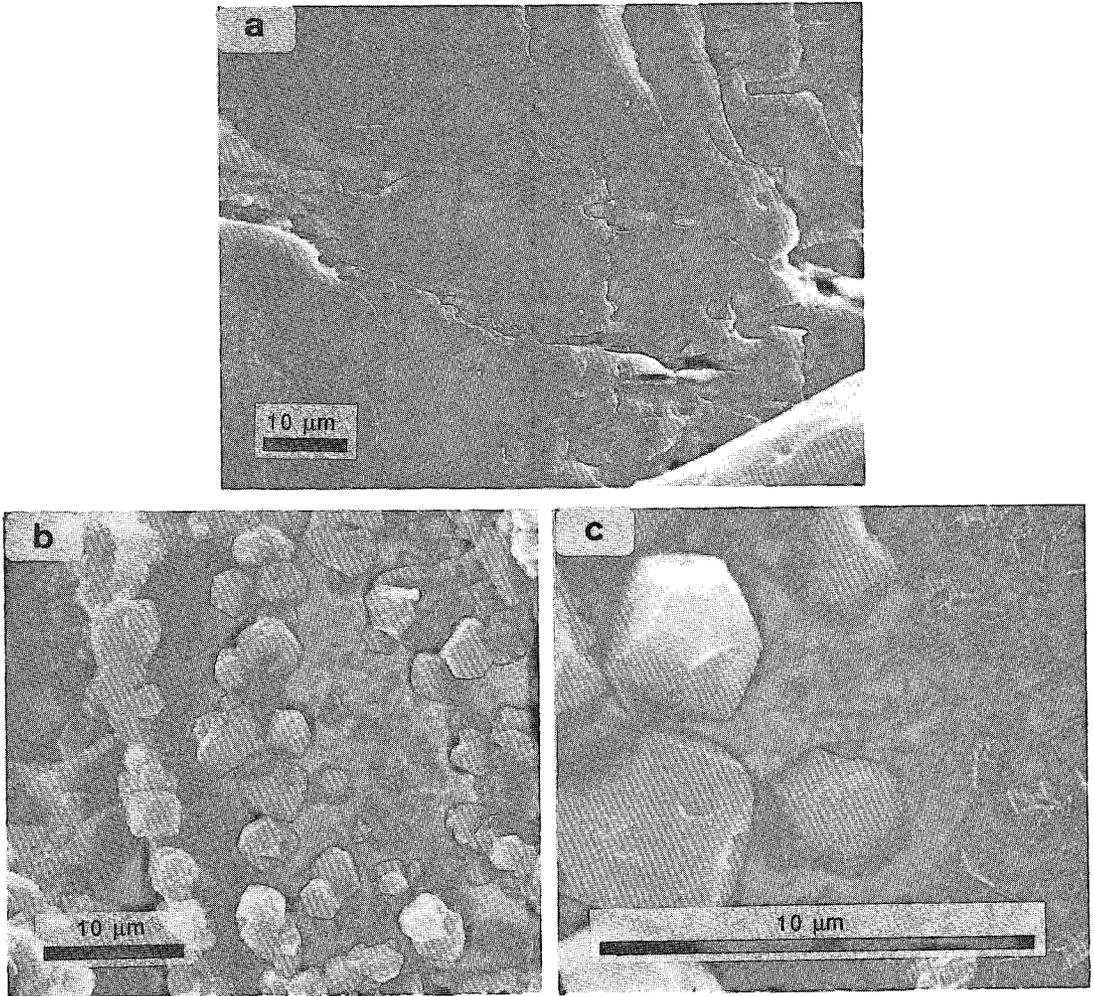


FIG. 6. SEM photomicrographs of nepheline and dolomite grains subjected to the ASTM C 289 Chemical Method. a: Nepheline showing extensive dissolution. b: Dolomite grain with its surface completely covered with idiomorphic calcite crystals and brucite flakes. c: Enlarged view of the central part of b.

(small size of particles, high temperature, *etc.*).

Other nonsilicate minerals were tested under the same conditions as those of the ASTM C 289 test. With calcite, some grains were slightly corroded, whereas others remained unaffected. This reflects the fact that the exposed area in contact with the solution was much greater in this experiment (about  $1.8 \text{ m}^2$ ) than the experiment with the epoxy resin mount (approximately  $2.5 \times 10^{-5} \text{ m}^2$ ). Since a limited amount of calcite can be dissolved in the NaOH solution, the grains that were not corroded when saturation was attained stayed that way. Intensive dedolomitization was again observed with dolomite, the grain surfaces being completely covered with calcite and brucite crystals (Figs. 6b, c). This time, cal-

cite crystals were observed, likely because the solution reached saturation with respect to this mineral, a phenomenon that did not occur in the first experiment at  $23^\circ\text{C}$ . Another carbonate mineral, siderite, was tested. SEM observations reveal extensive transformations of the grain surfaces. We could not clearly identify the nature of the reaction products using the EDX unit of the SEM. An X-ray-diffraction analysis revealed that akaganeite,  $\beta\text{-FeO}(\text{OH})$ , was the reaction product. In this reaction, iron is oxidized from the ferrous state in siderite to the ferric state in akaganeite. This reaction gives off  $\text{H}^+$  and affects accordingly the pH of the solution. This is in good agreement with the measured reduction of alkalinity ( $457 \text{ mmoles/L}$ ). Gypsum also was

completely transformed. In this case,  $\text{Ca}(\text{OH})_2$  was the reaction product, and there was no evidence of precipitation of sodium sulfate, which is much more soluble than lime. With goethite, no visible sign of reaction was observed (SEM and XRD).

In concrete, dolomite is usually innocuous (Fournier & Bérubé 1991), but in some argillaceous dolomitic limestones, it is closely associated with deleterious alkali carbonate reactions (Gillott 1964). Dolomite also was found to be reactive in the presence of lime, the same reaction products being observed (Bérubé *et al.* 1990). As these authors pointed out, the products of dedolomitization have a very low cementing capacity. Thus, in soil-lime stabilization, the presence of dolomite is undesirable because it consumes lime that otherwise would react with silicates to produce highly cementitious CSH. Siderite is not known to cause problems in concrete, but is rarely used. If its transformation to iron hydroxide takes place after the concrete has hardened, the associated increase in volume may lead to disruption of the concrete. Gypsum also may be deleterious in concrete, after the hardening is complete, by reaction with calcium aluminates in the cement paste to form fibrous ettringite, which is associated with an increase in volume (Dolar-Mantuani 1983). Since gypsum is usually carefully added to the cement to consume calcium aluminates during the hardening process, excess gypsum (from the aggregate) will probably react with the alkaline pore solution in concrete to precipitate portlandite, as observed in this study. Goethite is a stable form of iron hydroxide in the NaOH solution and, as observed, should not undergo noticeable chemical changes. The only reported concern with iron hydroxides is that they may hydrate further, with increase in volume (Dolar-Mantuani 1983).

As mentioned above, alumina and silica behave similarly in a NaOH solution. It would thus be helpful to measure the release of aluminum under the same experimental conditions, to provide a better understanding of the behavior of aluminous silicates such as nepheline and the feldspars. By combining the results for these two elements, a better solubilization ratio should emerge.

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