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Strätlingite formation in high-alumina cement–zeolite systems

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Reaction mechanisms of strätlingite formation in high-alumina cement (HAC)–zeolite systems were studied. A component separation method that made it possible to study individual reactions involving hydrated HAC and zeolite was employed. Different sodium salts, e.g. sodium silicate, sodium carbonate, sodium sulphate and sodium nitrate, were used to promote strätlingite formation in the HAC paste. Strätlingite forms preferentially to the cubic hydrogarnet phase in hydrated HAC systems in the presence of zeolite. A sufficiently high silicate concentration, arising from the dissolution of silica-bearing materials such as zeolite, is required. A high pH environment is also conducive to strätlingite formation. The thermochemical stability of CAH_{10} , the normal precursor to hydrogarnet formation, is apparently increased under the condition of high microsilica content.

Introduction

Strätlingite (C_2ASH_8) formation in high-alumina cement (HAC) has been reported.^{1,2} Strätlingite forms as a result of the reaction between aluminate and silicate phases. It was suggested that strätlingite formation might be responsible for the strength recovery after conversion of hexagonal phases to the cubic hydrogarnet phase, as it has relatively high strength. Microsilica has been reported to favour the formation of strätlingite.³ Granulated blastfurnace slag can also react with HAC phases, resulting in the formation of strätlingite.^{4–9} It was suggested that the reduction of strength in HAC due to conversion, which was attributed to strätlingite formation in preference to C_3AH_6 , might be preventable.

A new conversion-preventing additive system composed

primarily of a natural zeolite and a sodium salt has been developed at the National Research Council, Canada.¹⁰ It was reported^{11,12} that alkali ions can play a significant role in strätlingite formation in the HAC–microsilica system. Silica reacts to form silicates in a high pH environment. This reaction is accelerated in presence of an increased amount of alkali ions. The alkali ions may act as a catalyst activating microsilica surfaces. Silicate anions then react with hydrated calcium aluminates (C_2AH_8 or CAH_{10}) to produce strätlingite. Addition of sodium sulphate increases the pH value of the HAC–microsilica–water system to above 12.¹³ A pH value higher than 12 appears to be an indicator of strätlingite formation in the HAC–microsilica–water system.

Addition of a natural zeolite, comprising clinoptilolite, levyne and offretite, and one of four sodium salts to the HAC–water system (sodium sulphate, sodium nitrate, sodium silicate and sodium carbonate) was studied. The reaction mechanisms of strätlingite formation during hydration of HAC in the presence of these additives was of primary interest. Two classes of sample were considered

- (a) HAC slurry containing zeolite particulates and different sodium salts
- (b) zeolite slurry containing pre-hydrated HAC (H-HAC) particulates and different sodium salts.

Samples in each class were separated into two parts after two months' reaction: particulates and residual slurry. This process makes it possible to study the reactions involving H-HAC and zeolite individually.

Experimental details

Materials

These were

- (a) HAC: Ciment Fondu containing SiO_2 4.5%, CaO 39.8%, Fe_2O_3 11.3%, Al_2O_3 41.2%, MgO 0.6%,

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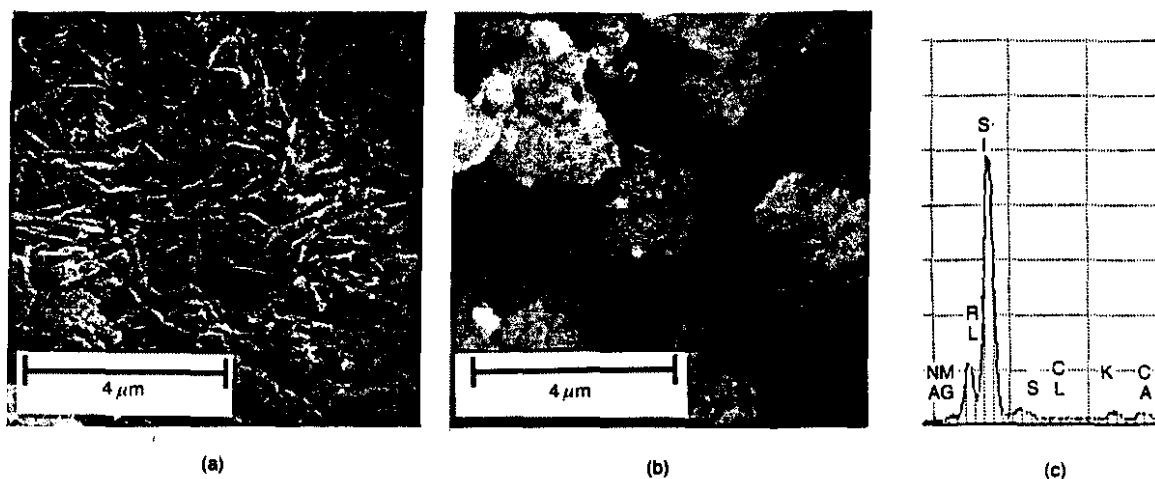


Fig. 1. The FEM/EDXA analysis for natural zeolite: (a) fracture surface of zeolite; (b) powdered zeolite; (c) EDXA spectrum

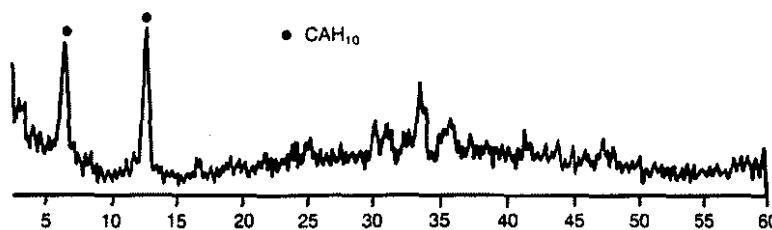


Fig. 2. The XRD pattern of H-HAC particulates

- $\text{Na}_2\text{O} + \text{K}_2\text{O} 0.1\%$, produced by Lafarge Calcium Aluminates
- (b) natural zeolite containing mainly clinoptilolite, levyne and offretite minerals, supplied by Zeotech Corp. (the SEM/EDXA analysis for the natural zeolite is shown in Fig. 1)
- (c) reagent chemicals: sodium sulphate, sodium silicate, sodium nitrate and sodium carbonate.

Sample preparation

H-HAC The HAC paste with water-cement ratio (w/c) = 0.6 was cast in $25 \times 25 \times 150$ mm steel moulds and cured at 0°C for 28 days. X-ray diffraction (XRD) analysis indicated that the main phase in the H-HAC paste was CAH_{10} , as shown in Fig. 2. The H-HAC paste was then ground and sieved into particulates of particle size between 1.168 and 3.327 mm.

Natural zeolite The natural zeolite rock was ground and sieved into two grades

- (a) powdered zeolite having particle size less than $75 \mu\text{m}$
 (b) zeolite having particle size of 1.168–3.327 mm.

Sample mixes are listed in Table 1.

Samples were placed in 100 ml bottles. Samples 1–4 (water-HAC ratio = 3) were hydrated at 38°C on a roller to prevent hardening. HAC slurry and zeolite particulates were separated by sieving each sample after 60 days' reaction. Samples 5–8 (water-zeolite ratio = 3) were placed at 23°C for 60 days. Zeolite slurry and H-HAC particulates were separated by sieving. The different curing temperatures employed provided a more favourable condition for possible strätlingite formation in each system. In the first case, 38°C favours strätlingite formation. In the second case, 23°C was used to avoid quick conversion from CAH_{10} to C_3AH_6 . If C_3AH_6 quickly forms and covers the surface of H-HAC particulates, reactions of the inner calcium aluminate phase with silicates from solution to form strätlingite will be restricted.

Table 1. Mixes (arbitrary mass units)

Sample	HAC	Particulate H-HAC	Powdered zeolite	Particulate zeolite	Admixture
1	1	—	—	1	0.05 sodium sulphate
2	1	—	—	1	0.05 sodium silicate
3	1	—	—	1	0.05 sodium nitrate
4	1	—	—	1	0.05 sodium carbonate
5	—	1	1	—	0.05 sodium sulphate
6	—	1	1	—	0.05 sodium silicate
7	—	1	1	—	0.05 sodium nitrate
8	—	1	1	—	0.05 sodium carbonate

The samples used in this study are divided into two classes as listed above: HAC slurry containing zeolite particulates and different sodiums, and zeolite slurry containing H-HAC particulates and different sodium salts. Samples in each class were separated into two parts after two months' reaction: particulates and residual slurry. The particulates were washed with water. The samples, i.e. slurries and particulates, were dried by vacuum in a desiccator at room temperature. Scanning electron microscopy (SEM) photographs and energy dispersion X-ray analysis (EDXA) spectra were taken on the surface of particulates or dried slurry powder. Ground powder of particulates or slurry was used for XRD analysis. A Rigaku X-ray diffractometer system Geigerflex D/Max-B was used for X-ray studies. A Cambridge Stereoscan S250 scanning electron microscope was employed for SEM/EDXA investigations.

Results

Class 1: particulate zeolite-HAC slurry-sodium salt systems

Zeolite particulates The XRD patterns, SEM photographs and EDXA spectra of zeolite particulates are shown in Fig. 3. The XRD showed little or no difference between the zeolite particulates immersed in HAC slurries containing different sodium salts for two months. The mineral composition of these zeolite particulates was the same as that of the natural zeolite. This indicated that no new reaction product formed on the zeolite particulates. It was clear in SEM photographs that the zeolite has a layered structure (Figs. 3(b)-3(e)). Zeolite particulates extracted from HAC slurries containing sodium silicate (Fig. 3(b)) or sodium nitrate (Fig. 3(e)) had clean surfaces. Small particles were found covering the surface of the zeolite particulates extracted from the slurries containing sodium carbonate (Fig. 3(c)) or sodium sulphate (Fig. 3(d)). EDXA spectra indicated that these particles are rich in calcium. The silicon and calcium peak intensities on clean surfaces were similar to those of natural zeolite. The silicon peak intensities of the sample surfaces covered with the small particles were apparently lower than for the natural zeolite; the calcium peak intensities were much higher. Deposits of calcium carbonate or calcium sulphate, which have relatively low solubilities, might be responsible for this phenomenon.

HAC slurries The XRD patterns, SEM photographs and EDXA spectra of HAC slurries containing different sodium salts are shown in Fig. 4. High strätlingite peak intensities were found in the XRD patterns of HAC slurries containing sodium silicate (Fig. 4(a)) or sodium carbonate. The strätlingite peak intensity in the HAC slurries containing sodium sulphate or sodium nitrate was relatively low. A calcium aluminium oxide carbonate hydrate phase ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$) was found in the sample containing sodium carbonate. The SEM photographs also showed more strätlingite plates in the first two samples than in the others (Figs 4(b)-4(e)).

Strätlingite plates were uniformly distributed among hydrogarnet (C_3AH_6) cubic particles. Dissolved silicates significantly affected the strätlingite and hydrogarnet formation. It was then apparent that more strätlingite formed in the HAC containing sodium silicate than in the others. A high pH value appeared to promote strätlingite formation. Sodium silicate and sodium carbonate are highly basic salts. More strätlingite formed in these samples. Hydrogarnet still formed in the systems studied at 38°C , since the amount of dissolved silicate from zeolite particulates was limited. Addition of sodium silicate apparently promoted strätlingite formation and reduced hydrogarnet formation.

Class 2: particulate H-HAC-zeolite slurry-sodium salt systems

Hydrated HAC particulates The XRD patterns, SEM photographs and EDXA spectra of H-HAC particulates after immersion in zeolite slurries containing different sodium salts are shown in Fig. 5. Strätlingite was detected in the particulates that had been immersed in zeolite slurries containing sodium silicate (Fig. 5(a)) or sodium carbonate for two months. The pH values of the zeolite slurries were determined by an Orion pH/ISE meter, model 720A. The pH values of the zeolite slurries containing sodium silicate or sodium carbonate were 12.59 and 12.50 respectively. Stellerite ($2\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 14\text{SiO}_2 \cdot 14\text{H}_2\text{O}$) was detected instead of strätlingite growing on H-HAC particulates under lower pH conditions. Samples were immersed in zeolite slurries containing sodium sulphate or sodium nitrate for two months. The pH values of these two slurries were 12.21 and 11.95 respectively. The CAH_{10} phase was present in all the samples after two months' curing in a silicate-rich environment at 23°C . No C_2AH_8 or C_3AH_6 was found. Ettringite formed on H-HAC particulates after immersion in zeolite slurry containing sodium sulphate. It is noted that ettringite formed only on H-HAC particulates (Fig. 5(d)) and not in the H-HAC slurry (Fig. 4(d)); the sulphate additions in these systems were the same. It has been reported that CAH_{10} forms ettringite more rapidly than other calcium aluminate hydrates.¹⁴ The particulate H-HAC was mainly composed of CAH_{10} ; ettringite might form from it at early ages. The effect of reaction site geometric location on ettringite nucleation/crystallization potential may also be a factor.¹⁵ The ettringite nucleation/crystallization potential is believed to increase in the following order.

in solution < on plate surfaces < in cracks

The SEM micrograph showed that needle-like ettringite crystals grew outwards from the particulate surface. Plate-like crystals were present in all the samples. The large crystals might be hydrated calcium aluminate. They were sites for strätlingite or stellerite crystal growth. Strätlingite and stellerite have plate-like morphology. No cubic hydrogarnet crystals were found in the samples by SEM.

Zeolite slurries The XRD patterns, SEM photographs

- Clinoptilolite, $(\text{Na, K, Ca})_8 \cdot (\text{Si, Al})_{36} \cdot \text{O}_{12} \cdot 20\text{H}_2\text{O}$
- Levyne, $\text{Ca}_3 \cdot \text{Al}_{6.5} \cdot \text{Si}_{11.5} \cdot \text{O}_{36} \cdot 18\text{H}_2\text{O}$
- Offretite, $(\text{K, Ca, Mg})_3 \cdot \text{Al}_{13} \cdot \text{O}_{36} \cdot 14\text{H}_2\text{O}$

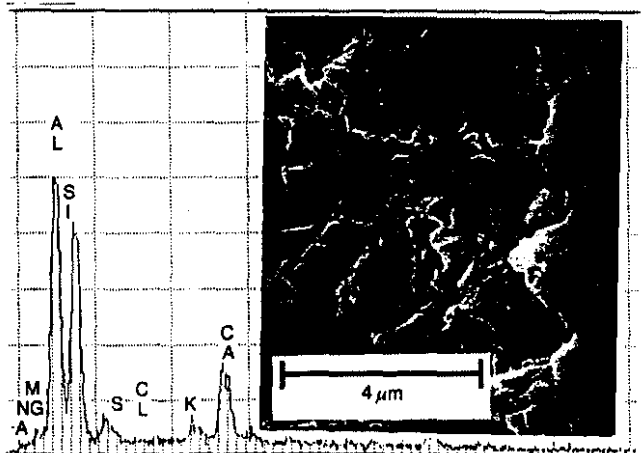
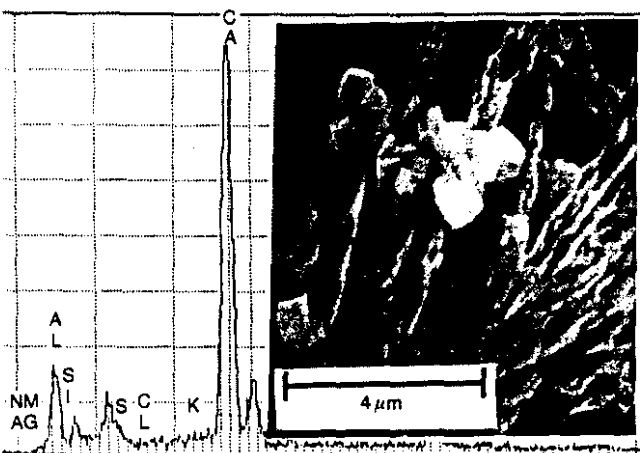
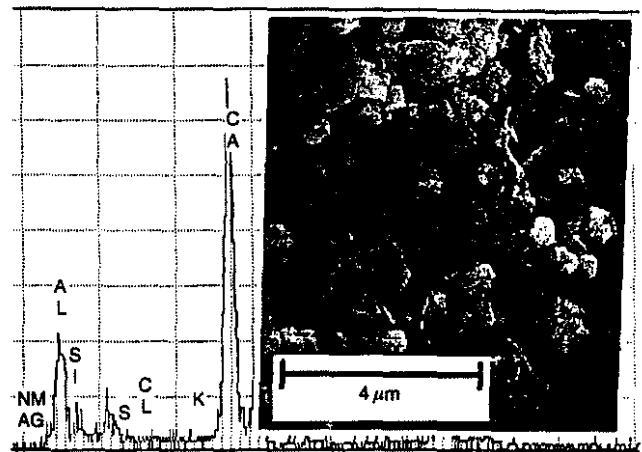
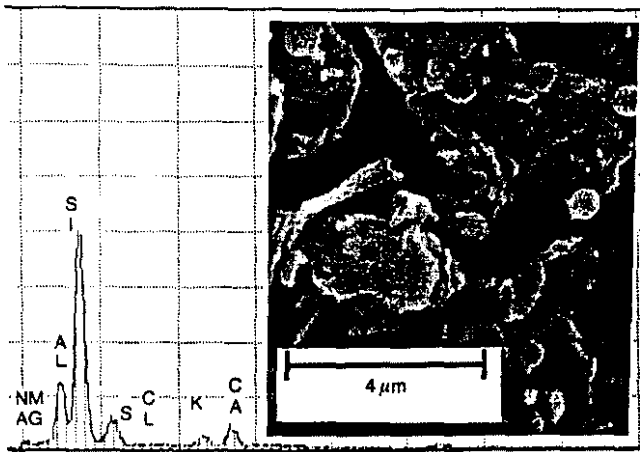
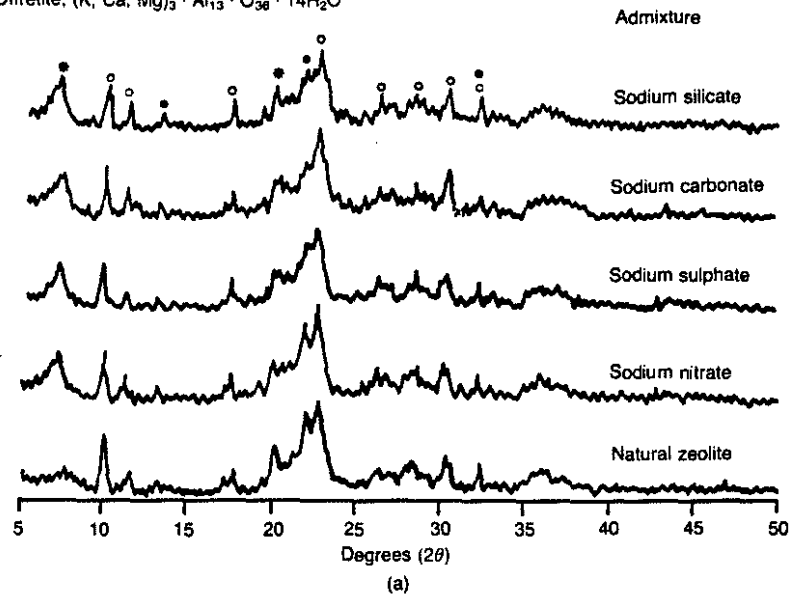


Fig. 3. (a) XRD patterns and (b)–(e) SEM/EDXA analysis of zeolite particulates after immersion in HAC slurries containing different sodium salts: (b) sodium silicate; (c) sodium carbonate; (d) sodium sulphate; (e) sodium nitrate

- $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 11\text{H}_2\text{O}$
- Strätlingite
- C_3AH_6

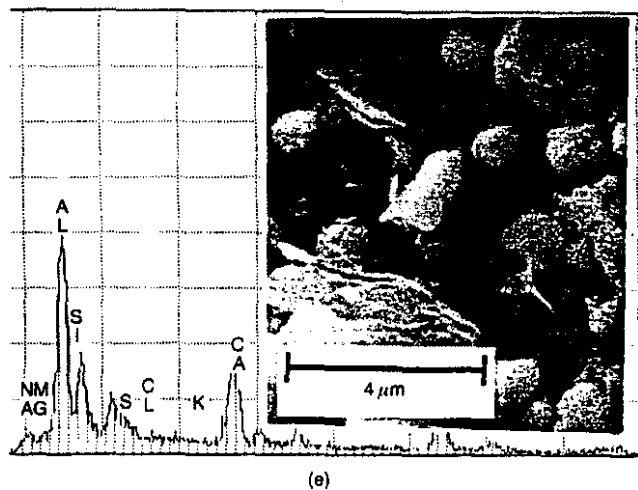
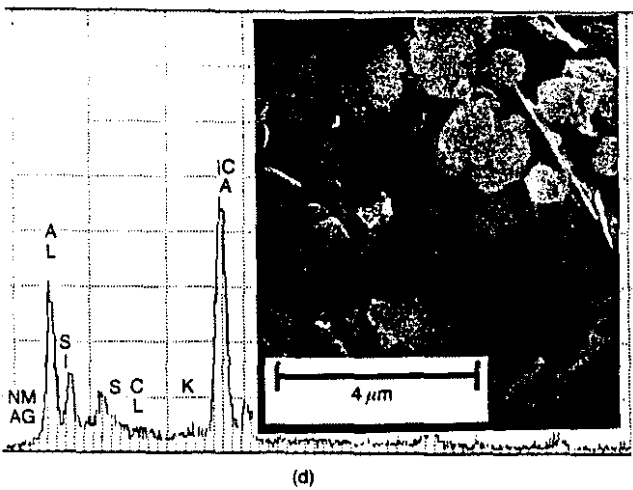
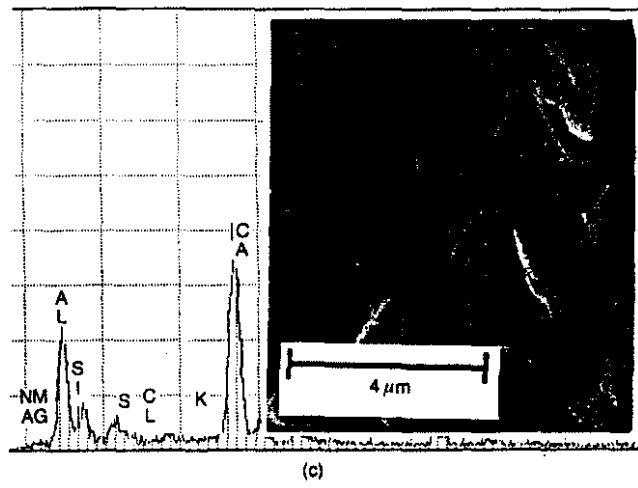
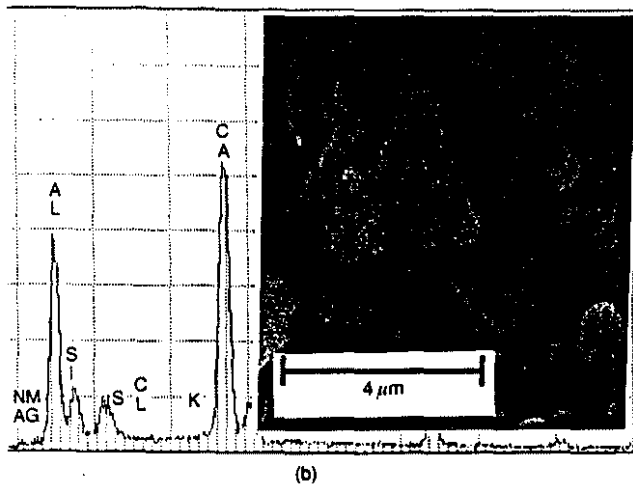
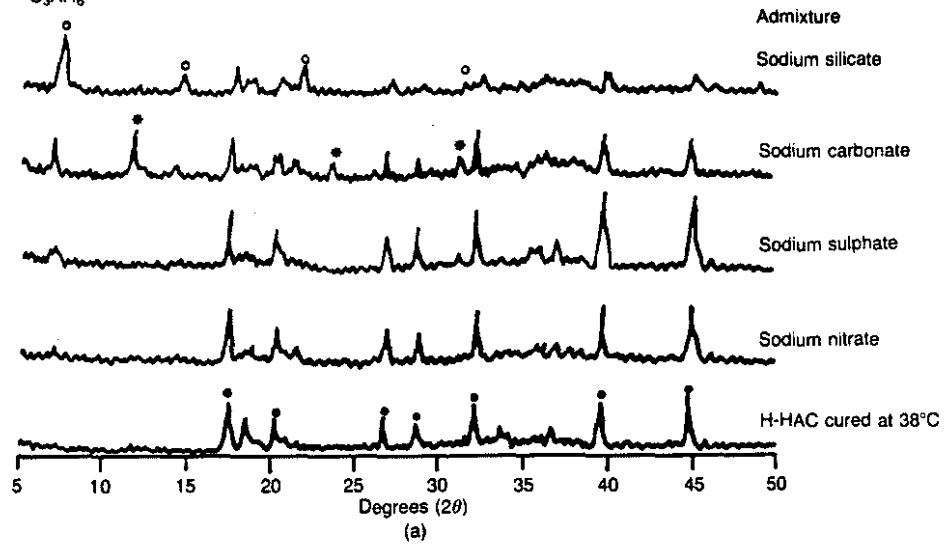


Fig. 4. (a) XRD patterns and (b)–(e) SEM/EDXA analysis of HAC slurries containing zeolite particulates and different sodium salts: (b) sodium silicate; (c) sodium carbonate; (d) sodium sulphate; (e) sodium nitrate

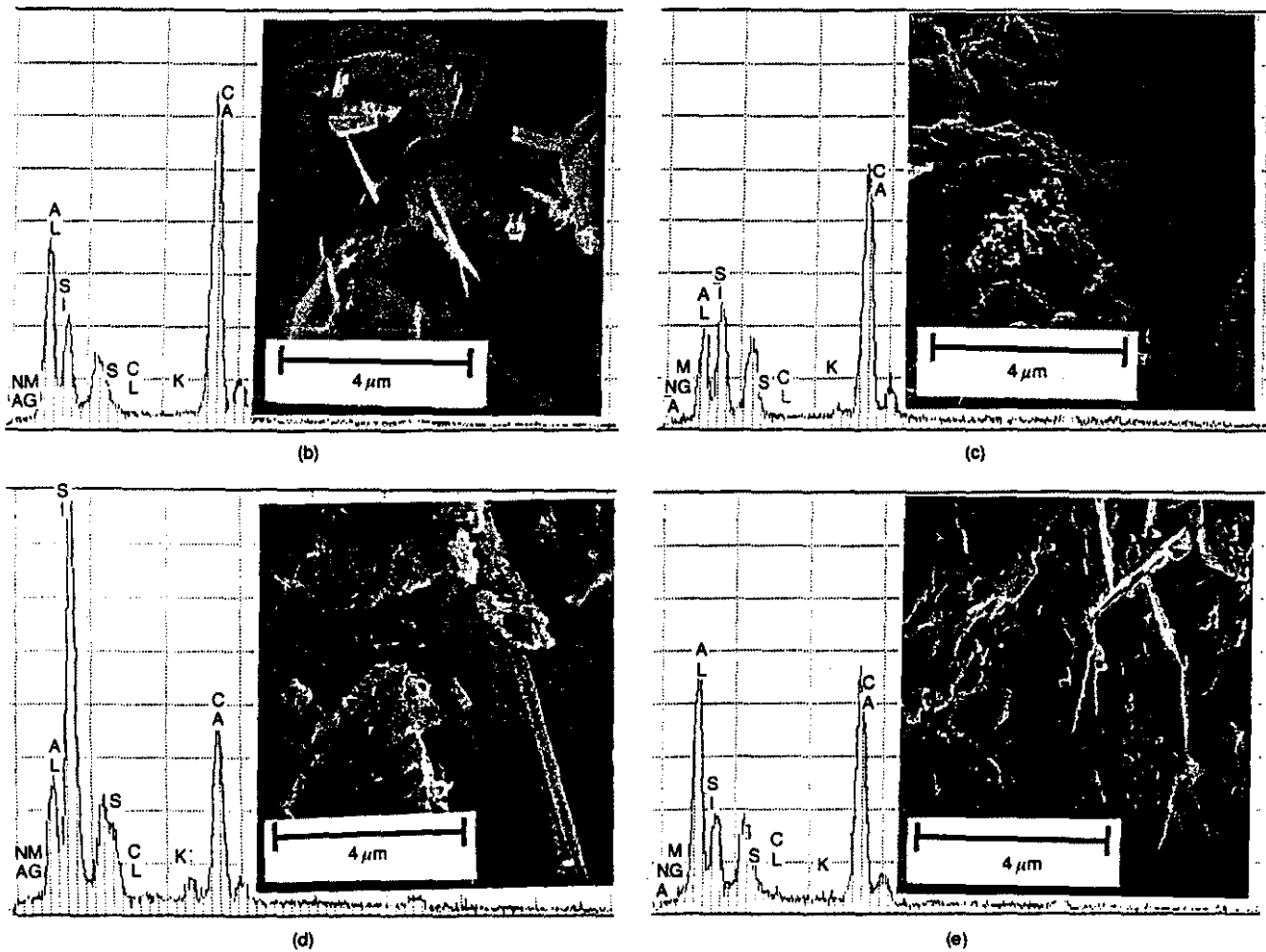
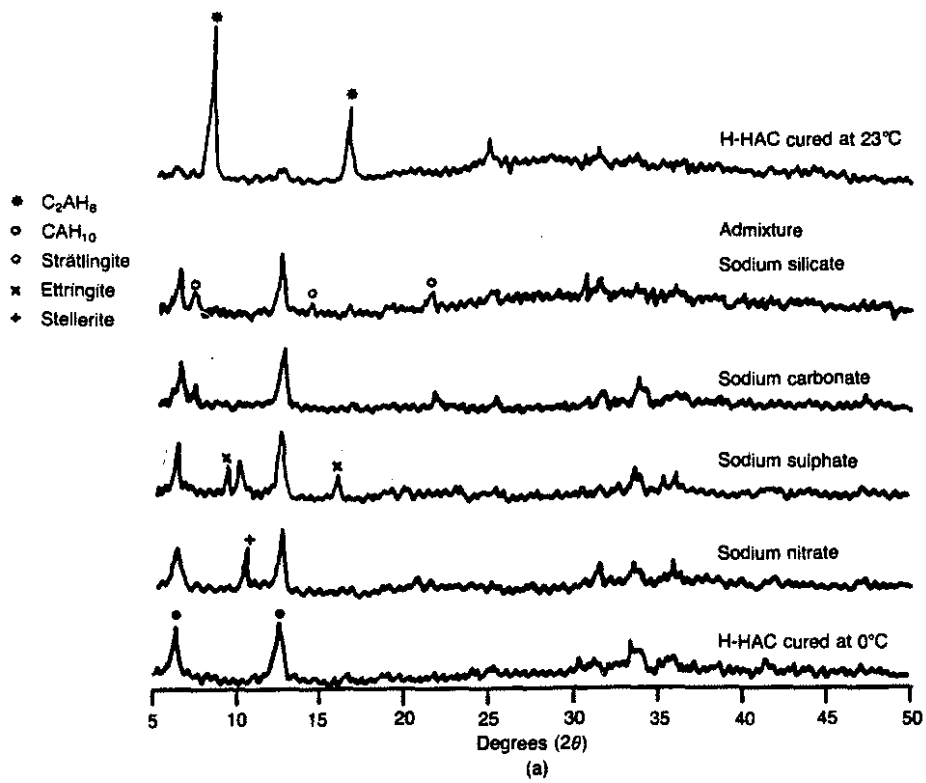


Fig. 5. (a) XRD patterns and (b)–(e) SEM/EDXA analysis of H-HAC particulates after immersion in zeolite slurries containing different sodium salts: (b) sodium silicate; (c) sodium carbonate; (d) sodium sulphate; (e) sodium nitrate

- Clinoptilolite, $(\text{Na, K, Ca})_8 \cdot (\text{Si, Al})_{36} \cdot \text{O}_{12} \cdot 20\text{H}_2\text{O}$
- Levyne, $\text{Ca}_3 \cdot \text{Al}_{6.5} \cdot \text{Si}_{11.5} \cdot \text{O}_{36} \cdot 18\text{H}_2\text{O}$
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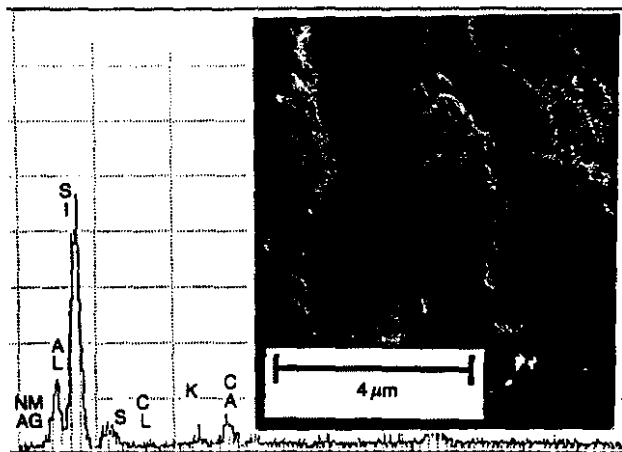
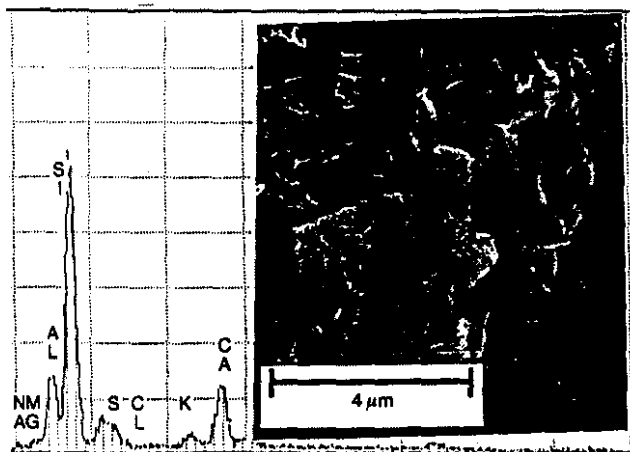
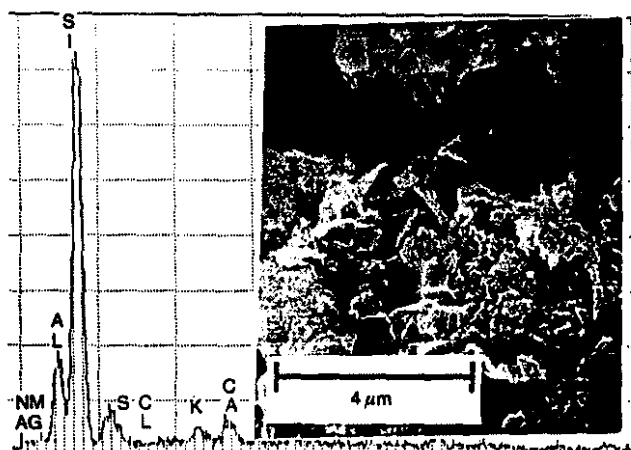
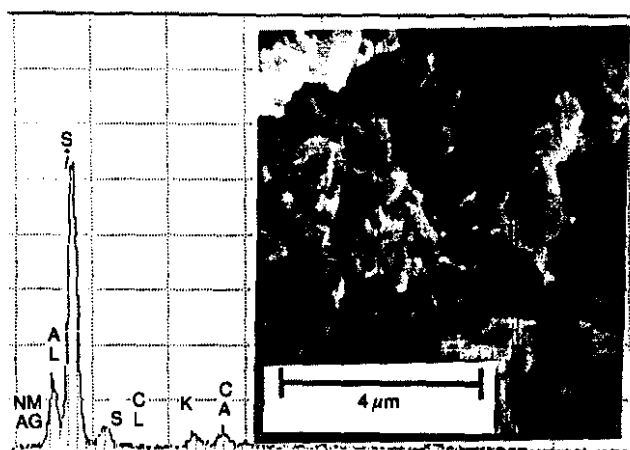
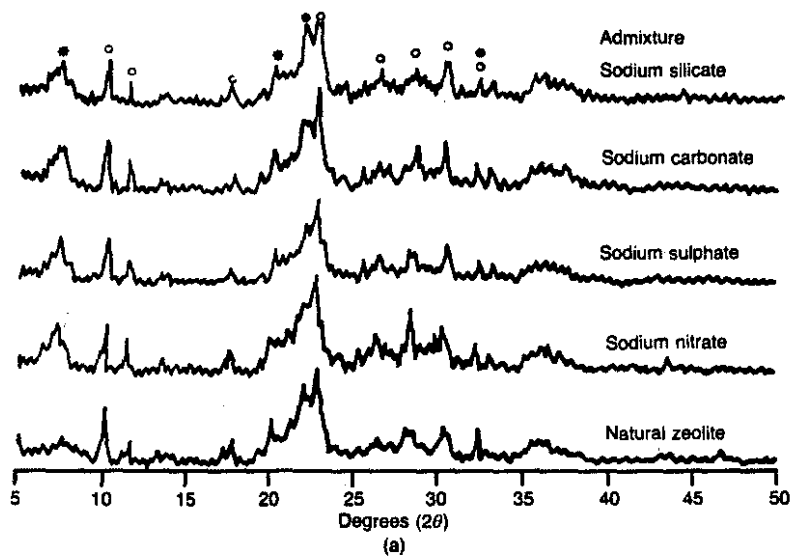


Fig. 6. (a) XRD patterns and (b)–(e) SEM/EDXA analysis of zeolite slurries containing H-HAC particulates and different sodium salts: (b) sodium silicate; (c) sodium carbonate; (d) sodium sulphate; (e) sodium nitrate

and EDXA spectra of zeolite slurries containing different sodium salts are shown in Fig. 6. The XRD pattern showed little or no difference between the zeolite slurries. The mineral compositions of the zeolite slurries were the same as that of natural zeolite, as shown in Fig. 1. No new reaction product appeared to form in the zeolite slurries. The EDXA spectra showed similar characteristics for all the samples. The zeolite slurries were conglomerated after drying. No hexagonal-plate or other reaction products were identified in the SEM photographs.

Discussion

Strätlingite appears to grow preferentially on hydrated HAC particles rather than on silica-bearing material, e.g. zeolite particles. The dissolved silicate concentration is relatively high in zeolite slurries containing H-HAC particulates (mainly consisting of CAH_{10}) and highly basic sodium salts, i.e. sodium silicate and sodium carbonate. Plate-like strätlingite crystals grow on the surface of H-HAC particulates. The dissolved silicate concentration is low in the HAC slurries containing zeolite particulates or agglomerates and different sodium salts. This is attributed to the small 'effective' reaction area of the zeolite agglomerates having relatively large size (1.168–3.327 mm in diameter); strätlingite is still formed and uniformly distributed in the HAC slurries. This phenomenon indicates that the reactions associated with strätlingite formation may take place topochemically on the surfaces of the H-HAC particulates. Dissolution of calcium aluminate phases appears to be more difficult than for zeolite. Zeolite releases silicate ions to the solution when activated by sodium ions. The dissolved silica then reacts with the calcium aluminate phase on the surface of the H-HAC particulates. Re-crystallization of the calcium aluminate phase occurs in the presence of sufficient silicate anions to form strätlingite. A relatively high pH environment, e.g. that resulting from addition of highly basic salts such as sodium silicate or sodium carbonate, appears to be more favourable for strätlingite formation. The solubilities of both zeolites and aluminates increase with pH. A lower pH environment appears to favour stellerite ($2\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 14\text{SiO}_2 \cdot 14\text{H}_2\text{O}$) instead of strätlingite formation. Stellerite is less basic than strätlingite since it contains more silica groups and less calcium oxide. This phase may not exist in real HAC products as it requires a relatively low pH condition.

The H-HAC particulates were made by hydrating HAC paste at 0°C . The hydration product was mainly CAH_{10} . CAH_{10} usually converts to C_2AH_8 at room temperature and to C_3AH_6 at elevated temperature, as it is thermochemically unstable. Test results indicate that the stability of CAH_{10} increases at low pH and high microsilica content. Reactions to form strätlingite or stellerite are believed to take place only in the outer layer of the H-HAC particulates. The core of the H-HAC particulates remains unchanged after two months' curing at room temperature. It is in the form of CAH_{10} .

Conclusions

1. Strätlingite appears to grow preferentially on hydrated HAC particles rather than silica-bearing particles.
2. A sufficiently high silicate concentration and pH environment is required for strätlingite formation in HAC paste.
3. The thermochemical stability of CAH_{10} is apparently increased at high microsilica content.

Acknowledgements

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Discussion contributions on this paper should reach the editor by 26 April 1996