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The effect of thiocyanates on the hydration of portland cement at low temperatures

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Abstract

Sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, calcium thiocyanate, and lithium thiocyanate were added to Normal Type 10 portland cement in amounts of 1.5 and 3% (with respect to cement on weight basis) and cured at temperatures of 20, 0 and −5°C. The rate of development of heat of hydration, calcium hydroxide content and strength development were followed from a few hours up to 28 days.

All thiocyanates increase the early rate of reaction of cement at 20°C. The most efficient early acceleration occurs with 3% $Ca(SCN)_2$. The total heat of hydration in samples containing KSCN is about 30% more than that registered for the reference at 3 days. At 0°C, there was acceleration in the presence of thiocyanates and the heat of hydration was higher in all the samples containing thiocyanates. All thiocyanates accelerate hydration at −5°C with respect to the reference paste. The reference sample showed practically no hydration even up to 4 days as the water in the pores remained frozen. Some freezing occurred in the presence of NH_4SCN, LiSN and 1.5% $Ca(SCN)_2$.

Calcium thiocyanate accelerates the hydration and strength development in the paste at all curing temperatures. It is the most effective thiocyanate for increasing strengths at low temperatures. After 28 days of curing at −5°C, the cement paste with 3% calcium thiocyanate attains a strength that is 74% of the strength of cement paste cured at 20°C. Sodium thiocyanate is also an effective accelerator and increases strength at low temperatures. The least effective thiocyanates with respect to the development of strengths at −5°C are LiSCN, KSCN and NaSCN at a dosage of 1.5%.

A linear relationship exists between the amount of lime formed and strength, within the range of curing periods studied. However, when strength is compared at the same degree of hydration (in terms of lime formed), some pastes exhibit better strengths than others. The relative strengths, therefore, seem to be dependent more on the microstructure of the pastes than on the degree of hydration. At the same degree of hydration at −5°C, 1.5–3% Ca thiocyanate, or 3% Na, K and Li thiocyanates exhibit better strengths than those containing 1.5% Na, Li and K thiocyanates.

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1. Introduction

Accelerating admixtures are added to concrete for reducing the time of setting and increasing the early strength development. They are used in cold-weather concreting operations and are also components of antifreezing admixtures and shotcreting mixes. The advantages derived by the use of these admixtures include: efficient start and finishing operations, reduction of the period of curing and protection, earlier removal of forms, plugging of leaks and acceleration of setting in shotcreting operations. Many organic and inorganic chemicals have been advocated for use as accelerators. The most efficient and economical acclerating admixture is known to be calcium chloride. A large amount of data is available on almost all aspects of the use of calcium chloride in concrete [1].

One of the limitations to the wider use of calcium chloride in reinforced concrete is that if present in larger amounts, it promotes corrosion of the reinforcement unless proper precautions are taken. Hence its use has diminished in recent years. Continued attempts are being made to develop an alternative admixture to calcium chloride. A number of organic and inorganic compounds have been suggested but none of them is as efficient and economical to use as calcium chloride. Much of the information is available only in the patent literature [2]. One of the accelerators that is available commercially is based on formates. They are not as efficient as the chloride and are also more expensive. Calcium formate, for example, has a limited solubility in water and when added as a powder, creates some dispensing problems. The effectiveness of calcium formate depends to some extent on the C_3A/SO_3 ratio. Sodium formate is more soluble than the calcium salt but, because of its sodium content, if used in large amounts could result in an enhancement of the alkali-aggregate expansivity.

Another chemical that has been suggested as an accelerator is sodium thiocyanate. It has been shown to accelerate the hydration of cement [3, 4]. Rear and Chin [5] found that at 10°C, concrete containing sodium thiocyanate had higher strengths than that of the reference. Brook et al. [6, 7] have provided data on the effect of cold-weather admixtures on strengths. Some work has also been reported on the effect of sodium thiocyanate on the corrosion of reinforced steel [8, 9].

Although sodium thiocyanate is an accelerator, it is possible that at higher dosages it might increase the alkali content in concrete which may not be desirable when using certain aggregates. There is, hence, a need for information on the effect of non-sodium-containing thiocyanates on the properties of cement pastes. A literature survey indicates that there is no detailed information on research pertaining to the effect of sodium-free thiocyanates on the physico-chemical characteristics of cement pastes hydrated at low temperatures.

An investigation was carried out to evaluate the relative effects of sodium, potassium, ammonium, calcium and lithium thiocyanates on the hydration and strength development in cement pastes cured at 20, 0 and -5°C for periods up to 28 days. Another objective of this study was to determine the most suitable thiocyanate, so that it could be combined with a suitable freezing-point depressant to produce an efficient multifunctional antifreezing admixture.

2. Experimental

2.1. Materials

2.1.1. Portland cement

Normal Type 10 portland cement, manufactured by Lafarge Canada, Inc., was used, at a water–cement ratio of 0.25. The compound and oxide analyses are given in Tables 1 and 2.

Table 1
Compound analysis of type 10 portland cement*

Compound	
Tricalcium silicate (C_3S)	48.4%
Dicalcium silicate (C_2S)	24.5%
Tricalcium aluminate (C_3A)	6.8%
Tetracalcium aluminoferrite (C_4AF)	8.4%
$CaSO_4$(SO_3 equivalent)	4.2%
Total	92.3%

* Cement nomenclature: C, CaO; S, SiO_2; A, Al_2O_3; F, Fe_2O_3.

Table 2
Oxide analysis of type 10 portland cement

Oxide	Percentage
Silica	21.82
Alumina	4.05
Titania	0.22
Ferric oxide	2.77
Calcium oxide	62.49
Magnesium oxide	3.69
Sodium oxide	0.12
Potassium oxide	0.44
Sulfur trioxide	2.48
Ignition loss	1.90

2.1.2. *Thiocyanates*

Sodium thiocyanate (NaSCN), potassium thiocyanate (KSCN), ammonium thiocyanate (NH_4SCN), calcium thiocyanate ($Ca(SCN)_2$), and lithium thiocyanate (LiSCN) were used in concentrations of 1.5% and 3% by weight of cement. Stock solutions of the thiocyanates containing 6 and 12% of the thiocyanate (by weight of solvent) were prepared from the solid form, with distilled water as the solvent.

2.2. *Techniques and procedures*

2.2.1. *Isothermal conduction calorimetry*

Conduction calorimetry measures the rate of heat and the total heat evolved during hydration as a function of time at a constant temperature. The calorimetry unit consisted of six cells, each equipped with a heat flow meter, mounted on an insulated base plate. The unit was sealed with a rubber O-ring, vacuum grease and an aluminum cover to prevent ingress of water. The calorimeter was submerged in an isothermal water bath immediately after samples were weighed into the cells. The heat flow meters measured the heat production, and these voltage signals were recorded by a data logger.

Solutions containing 0, 1.5 and 3% thiocyanate by weight of cement were added to 10 g of cement at a water-cement ratio of 0.25. This ratio is sufficient to hydrate the cement completely and also provides good workability. The samples were mixed by hand and placed immediately into the calorimeter. The apparatus was sealed and placed in the water/ethylene glycol bath. Experiments were performed at bath temperatures of 20 ± 0.01°C, 0 ± 0.1°C and -5 ± 1°C. Voltage signals were recorded every 10 min for 72-96 h.

2.2.2. *Derivative thermogravimetric analysis (DTG)*

DTG measures the rate of weight change of a material as a function of temperature. The degree of hydration of sample can be estimated by determining the weight loss of water due to the decomposition of calcium hydroxide. This weight loss due to the decomposition of $Ca(OH)_2$ occurs at about 400°C and is determined by calculating the area under the weight loss differential curve. From the weight loss, the amount of calcium hydroxide present in the paste is computed.

Fragments of cubes from the compressive strength measurements were dried in a vacuum oven at 110°C for 1 day, then finely ground with a mortar and pestle; 25 ± 1 mg of the sample was placed on the pan and inserted into the furnace. The sample was heated from room temperature to 1000°C at a rate of 20°C min^{-1} by the DuPont thermogravimetric analyzer in a continuous flow of nitrogen (100 ml min^{-1}). The rate of weight loss and the total weight loss were recorded every 3s.

2.2.3. *Compressive strength tests*

Cubes were subjected to loading by a Tinius Olsen Testing Machine, as outlined in ASTM standard C109, at a constant rate until failure.

Paste cubes of 50.8 mm length were mixed according to ASTM Standard C305 and prepared and tested according to ASTM Standard C109. A water- cement ratio of 0.25

was employed at thiocyanate concentrations of 0, 1.5 and 3% by weight of cement. Cubes were stored at temperatures of 23°C (humid room), 0°C and −5°C (chest freezers) for the entire curing period. Tests were performed after 1, 2, 3, 7, and 28 days of curing.

3. Results and discussion

The calorimetric curves for the rate of heat development and the total heat evolved at each temperature are shown in Figs. 1–3. The curve representing the sample containing no admixture is plotted on each graph as a reference. The reference exhibits a peak at about 10 h representing the hydration effect of the C_3S phase. There is also a second peak effect at about 14 h signifying the reaction of the C_3A phase.

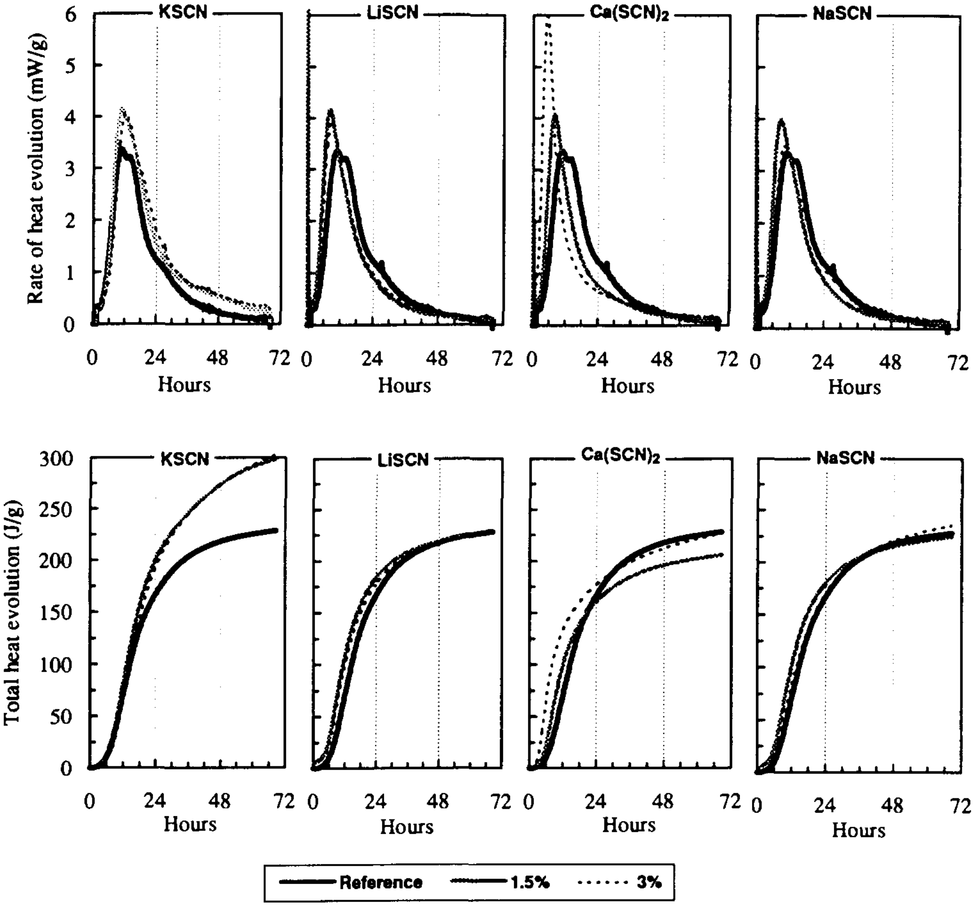

Fig. 1. Heat of hydration curves of cement paste with salts of different concentrations at 20°C.

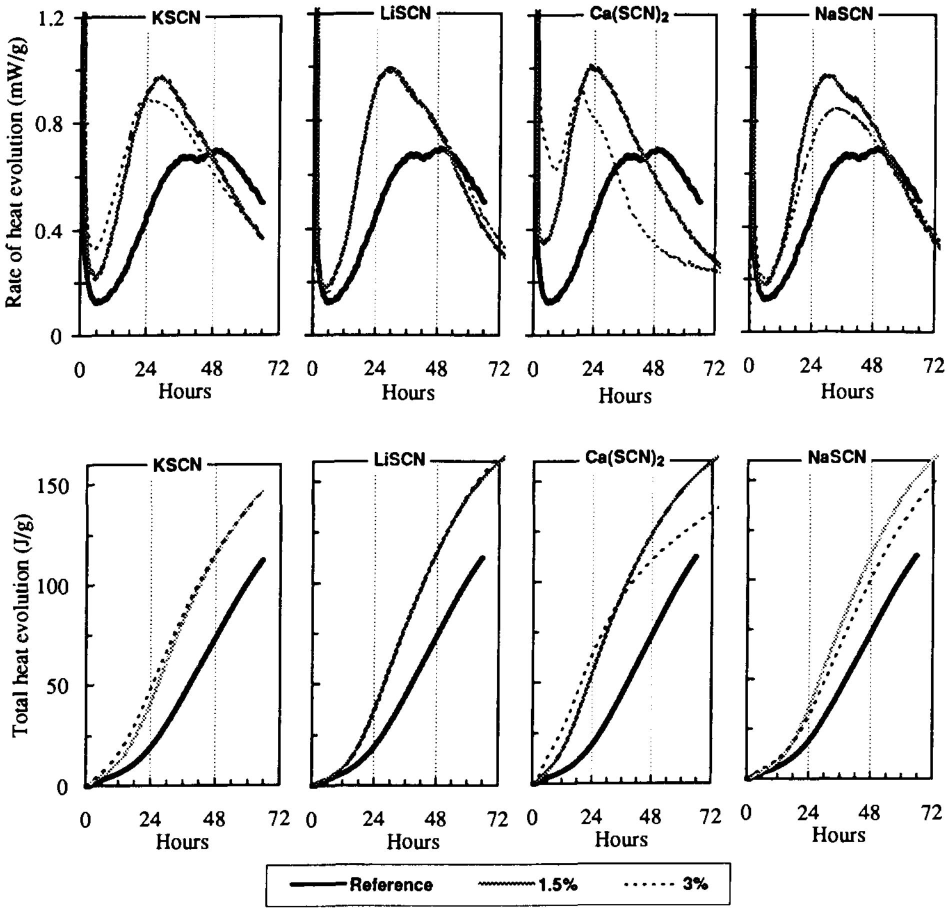

Fig. 2. Heat of hydration of cement paste with salts of different concentrations at 0°C.

At 20°C, all thiocyanates initially increase the maximum rate of heat evolution and shift the occurrence of the peak to earlier times by 1–6 h (Fig. 1). The KSCN-containing sample shows a higher rate of heat production than others even after 24 h. Thus KSCN may be termed a sustained accelerator. There is evidence that in most samples there is a reduction in the induction period. Higher concentrations of salts do not necessarily reflect in an earlier peak occurrence or higher rate of heat production. Of the thiocyanates, $Ca(SCN)_2$ shows the largest increase in the rate of heat production and the earliest occurrence of the C_3S peak at a dosage of 3% (Fig. 1). The effect of the thiocyanates on the first aluminate peak cannot be discerned as the calorimeter took an hour to equilibrate after the placement of the samples, by which time most of the reaction has occurred. The second increase in the rate of heat evolution due to the formation of low sulfoaluminates is not detected in any of the curves of the samples with

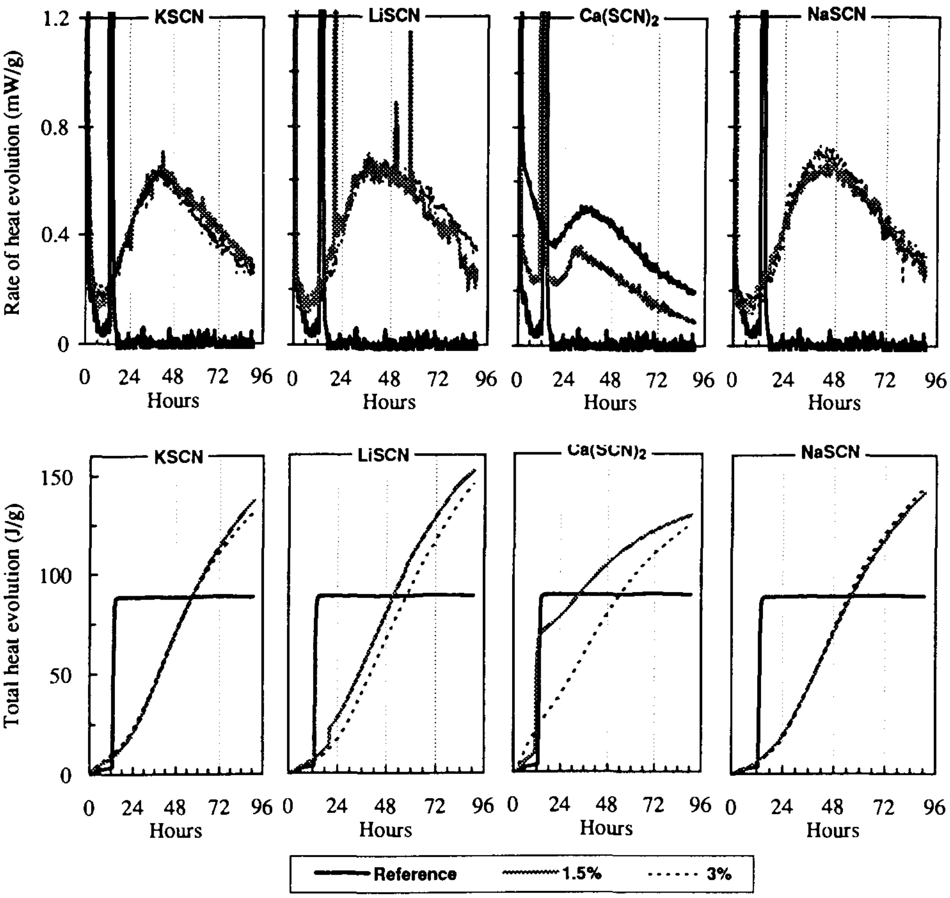

Fig. 3. Heat of hydration curves of cement paste with salts of different concentrations at −5°C.

salts, but is observed in the reference curve. Possibly this effect is accelerated in the presence of the accelerators and is masked by the C_3S peak.

The total amount of heat production for all samples reaches the same value at about 3 days, the KSCN-treated sample being the exception. After 3 days, the total heat produced by KSCN addition is 30% higher than that of the reference, indicating that KSCN, although a weaker accelerator initially, continues to accelerate the hydration of cement over a longer period. Some admixtures may not decrease the induction period but do act as late accelerators. The nucleation effects after the initial hydration may account for this behavior [10].

Fig. 2 refers to the calorimetric curves for samples hydrated at 0°C. The peaks are not as sharp as those obtained at 20°C. The maximum rate of heat production for the reference at 0°C is 20% of that at 20°C. This is expected, as the rate of hydration is lower at 0°C. After 3 days, the amount of total heat developed at 0°C by the reference sample is about 50% of that developed at 20°C. There is no indication of freezing of water in any of the specimens. In addition to the freezing-point depression due to the salts present, even in the reference samples, some heat due to hydration at this temperature may prevent freezing.

The induction period for all the samples containing thiocyanates is decreased, indicating that hydration is accelerated. The C_3S peak appears several hours earlier than that of the reference in the presence of thiocyanates.

The total heat evolved in most samples is about 30% or higher than that of the reference after 3 days, with the exception of samples with 1.5% NH_4SCN, which dips below the reference after 2 days (not shown). At the earlier period, $Ca(SCN)_2$ seems to accelerate hydration better than other thiocyanates. At about 3 days, the amount of heat developed is similar in all samples (except NH_4SCN) containing thiocyanates and the values are higher than those of the reference. By comparing the relative accelerating effects at the same temperatures, there is indication that the accelerating action of a thiocyanate is more pronounced at 0°C than that at 20°C.

Heat evolution curves for samples hydrated at −5°C are given in Fig. 3. Only the paste with LiSCN showed intense inflections between 48 and 60 h, indicating the possibility of some isolated freezing effects. The total heat of hydration is not affected by these inflections. The reference sample freezes after 14 h, as seen by the sharp increase in the rate of heat evolved. After this freezing, the rate falls to zero and little hydration occurs. The heat curve reaches a value of about 20 cal g^{-1}, which when converted to a value representing the mass of water in the sample, corresponds to the heat of fusion of water (80 cal g^{-1}). No hydration occurs after freezing. Therefore most of the cement remains unhydrated for the period studied.

Samples containing NaSCN and KSCN (Fig. 3) show gradually increasing rates of heat development with a maximum rate of reaction at 40 h. The total heat evolved gradually increases with time for the NaSCN and KSCN samples, indicating that freezing does not occur in these samples. The addition of salt depresses the freezing point and also accelerates the hydration of cement.

A gradual increase in the heat development can be seen in the curve representing 3% LiSCN, as well as with 1.5% LiSCN, with a small steep step with the latter, implying partial freezing of water in the pores at a lower concentration (Fig. 3). However, hydration continues in these samples, due to the acceleration effect.

NH_4SCN addition results in an anamolous effect (not shown). The heat evolution curve of 3% NH_4SCN increases then levels off, indicating that little hydration products are forming; possibly it froze within 2 h of placement into the calorimeter. One possibility is that a better acceleration of cement hydration occurs at a dosage of 1.5% than at 3.0%, thereby countering the freezing effect. At 0°C, there is indication that 1.5% NH_4SCN develops more heat than 3.0% NH_4SCN.

At 1.5% $Ca(SCN)_2$, freezing occurs at 12 h, resulting in a heat increase of 14 cal(g cement)$^{-1}$. After this, the slope of the total heat curve is positive, indicating continuation of hydration. At 3% $Ca(SCN)_2$, there is no indication of freezing and acceleration of hydration is therefore evident.

In summary, the conduction calorimetric curves indicate that all thiocyanates are accelerators at 20°C. The best accelerator in the first few hours is Ca thiocyanate at a dosage of 3%. A sustained acceleration up to 72 h is shown by KCSN at 1.5–3.0% dosage. Ammonium thiocyanate accelerates to the least extent. At 0°C there is no evidence of freezing of water in any of the samples, including the reference. This means that the salt concentration even in the reference is enough to prevent freezing from occurring. The acceleration effect at 0°C is more efficient than that at 20°C. Ammonium salt is the least effective and the calcium salt the most effective accelerator, at earlier times. At 3 days, Na and Ca thiocyanates produce about 70% of the total heat produced by the reference at 20°C. At −5°C, water in the reference specimen froze and there was no hydration. Some freezing seems to occur in samples containing 1.5% Ca, Li and NH_4 salts but this does not prevent continued hydration. The samples with 3% Ca thiocyanate and LiSCN exhibit the highest total heat at −5°C (at about 4 days) and is more than 50% of that produced at 20°C. Contrary to expectation 1.5% NH_4 salt showed a better accelerating effect than 3%.

The compressive strengths of samples cured at room temperature, as well as other temperatures, are compared in Figs. 4 and 5. At 20°C, after 1 and 2 days curing, the samples with thiocyanates generally attain strengths that are 5–10 MPa lower than that of the reference. One exception is $Ca(SCN)_2$ paste which has a strength equal to cement paste with no thiocyanate. The strengths are not related to the amount of heat developed at 1 day. The total porosity may be an important factor determining strength. The KSCN paste, although producing the largest amount of heat, develops

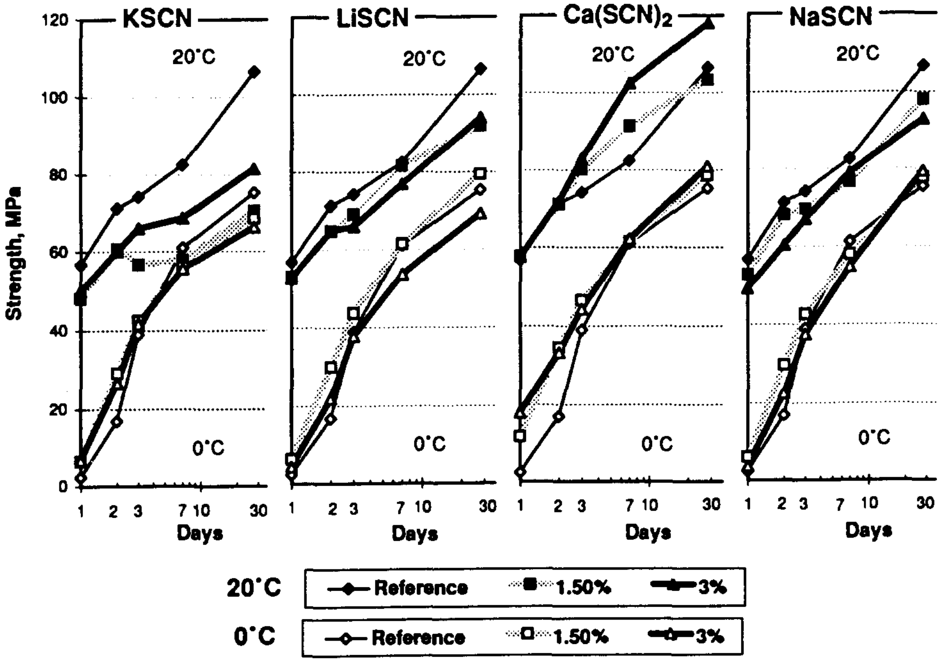

Fig. 4. Compressive strength of paste cubes with salts of different concentrations hydrated at 0 and 20°C.

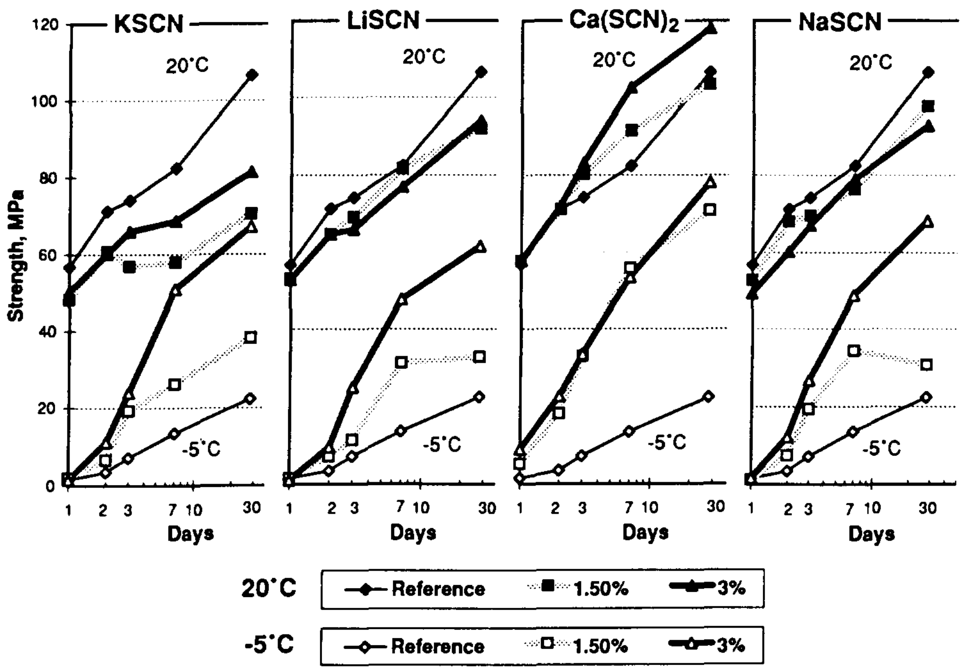

Fig. 5. Compressive strength of paste cubes with salts of different concentrations hydrated at −5 and 20°C.

relatively lower strengths compared to others. In the hydration of tricalcium silicate with NaOH, it has been found that the strengths of the reference pastes are higher than those containing NaOH, although the rate of hydration is accelerated by NaOH. One of the explanations is that in the pastes containing NaOH, a poor bond forms between the low surface area platy structure. A fibrous matrix is formed in the reference paste that develops better strengths [11]. At 3 days, the strength of samples with 1.5% NH_4SCN and $Ca(SCN)_2$ surpasses that of the reference. The samples containing KSCN, LiSCN, and NaSCN have strengths 3–14 MPa lower than those of the reference value. At this period KSCN paste, although producing a larger amount of heat than the others, does not show higher strengths. The porosity of the paste containing KSCN is possibly larger than that of the others.

At one week, pastes with 1.5% NH_4SCN and $Ca(SCN)_2$ produce higher compressive strengths than the reference. The weakest sample results are within KSCN, attaining 70–80% of the reference strength. The compressive strength of the reference cement paste at 28 days is 107 MPa. The $Ca(SCN)_2$ sample has a strength of 96 and 109% of this value for concentrations of 1.5 and 3% respectively. The KSCN sample achieves 66 and 76% of the reference value, LiSCN, 86 and 88%, and NaSCN, 92 and 87%. With 1.5% NH_4SCN, the sample reaches 95% of the reference strength.

Compressive strength measurements for samples containing NH_4SCN were discontinued due to the production of strong vapor associated with the preparation of the samples.

All samples, as would be expected, had lower strengths at the curing temperature of 0°C than at 20°C. At 1 day, all cubes cured at 0°C containing thiocyanates have strengths greater than those of the reference, as shown in Fig. 4. The specimen with $Ca(SCN)_2$ in particular, had strengths 5 to 7 times that of the sample containing no admixture. At 2 days, all cubes continue to have higher strengths than those of the reference. The samples with 1.5 and 3% $Ca(SCN)_2$ attain at 3 days, 18 and 13% higher strengths than the reference. At 7 days the strengths of these samples are similar to those of the reference and that with 1.5% LiSCN. At 28 days, samples with 1.5% LiSCN, 1.5% NaSCN, 3% NaSCN, 1.5% $Ca(SCN)_2$ and 3% $Ca(SCN)_2$ have strengths higher than that of the reference (75 MPa), while those containing 1.5% KSCN, 3% KSCN and 3% LiSCN have slightly lower strengths.

$Ca(SCN)_2$ is the most effective thiocyanate for accelerating strength gain and maintaining higher strengths throughout the 0°C curing period. 1.5% LiSCN and 1.5% NaSCN also appear to have a beneficial effect on strength gain at 0°C. KSCN produces higher early strengths than the reference but lower values at later ages. After 1, 2, 3, 7 and 28 days, the reference specimen cured at 0°C has 4, 24, 53, 74 and 71% of the strength obtained at 20°C. The addition of 1.5% $Ca(SCN)_2$ elevates these values to 32, 48, 63, 74 and 74%, respectively.

After 1 day of curing at −5°C, the reference and other samples with thiocyanates have approximately the same breaking strength of 1.5 MPa, except for those with 1.5% and 3% $Ca(SCN)_2$, which have strengths of 5 and 9 MPa respectively (Fig. 5). The reference sample cured at −5°C attains only 3% of the strength of that attained at 20°C in one day. It is very difficult to determine the precise breaking strength of the −5°C reference due to the large deformation of the cube during loading. After 2 days, the strengths of the cubes with thiocyanates are twice those of the reference. The addition of $Ca(SCN)_2$ results in values reaching 5 to 7 times those of the reference. This trend is valid at 3–7 days of curing.

Although the reference cubes freeze at −5°C, some strength is gained over time. This is due to the existence of some unfrozen water promoted by the presence of the salts. The solid ice present in the pores may also slightly promote strength development. There was evidence that stresses created due to the expansion of ice crystals caused areas of weakness along which failure occurred. Concentrations of 3% thiocyanate are more effective for accelerating strength development than 1.5% for all salts cured at −5°C. The pastes with 1.5 and 3% $Ca(SCN)_2$ exhibit almost similar strength values.

After 28 days, at additions of 3% $Ca(SCN)_2$, 3% NaSCN, 3% KSCN, and 3% LiSCN, strengths are 3.3, 3.1, 3.0, and 2.8 times those of the reference value at −5°C. These strengths are respectively, 74, 64, 63, and 58% of the strengths of the reference specimens hydrated at room temperature. $Ca(SCN)_2$ is the most effective of the admixtures in accelerating the strength gain at −5°C, 1.5% LiSCN, KSCN and NaSCN being less effective. Earlier work [12] on chlorides containing cations such as Ca, Sr, Ba, Li, Na and K has shown that the best accelerating cation is Ca. The accelerating effect of the cations was in the decreasing order $Ca > Sr > Ba > Li > Na > K$ [13]. It appears that the formation of the initial metastable hydration products on the hydrating silicate surface as well as the nucleation processes are influenced by the nature of the cations.

The strength development is a complex function of the acceleration effect of the thiocyanates on the hydration of cement, the pore structure of the pastes, its microstructure and the degree to which the freezing of water occurs.

One of the methods of following the rate of hydration of cement is through the estimation of calcium hydroxide formed at different times. This is not an accurate method but yields the relative rates of hydration of cement containing various thiocyanates. The percentage of calcium hydroxide (CH) present in each cube was determined on the ignition loss basis. In Figs. 6–8, all the lines are plotted in the same figure because basically the data can be divided into three sets, i.e. the reference material, that containing calcium thiocyanate, and all the others. Most samples showed increasing amounts of CH with the progress of hydration (Figs. 6–8).

Samples cured at room temperature contained between 5 and 12% CH. After 1 day, all samples had equal or lower amounts of CH than the reference. The lowest amount of CH was found in the NH_4SCN sample at 5.6%. After 2 days, NH_4SCN still contained the least amount of CH. The only sample that showed a greater amount of CH than the reference was that with 1.5% NaSCN. Almost all samples contained similar amounts of CH after curing for 1 week. After 28 days, all salts except 1.5% NH_4SCN and 3% $Ca(SCN)_2$ increased the amount of lime over the reference. These results in most cases are in conformity with those obtained by conduction calorimetry.

Curing at 0°C results in a lower degree of hydration at each hydration period compared to that cured at 20°C. Samples contained between 2 and 10% CH. Addition of thiocyanates increased the CH content over the reference at 1 day. This is also

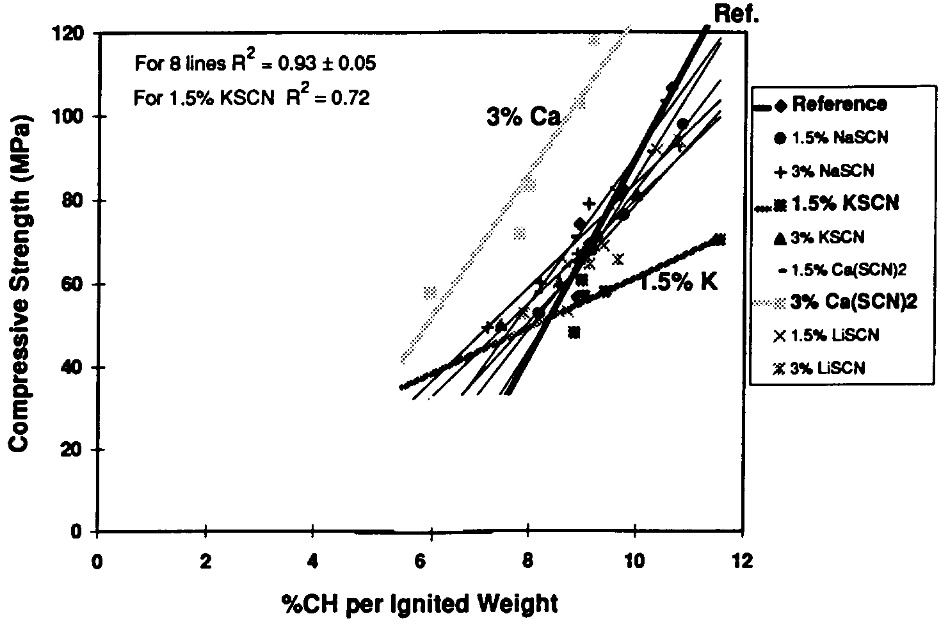

Fig. 6. Relationship between strength and % calcium hydroxide in cement paste hydrated at 20°C.

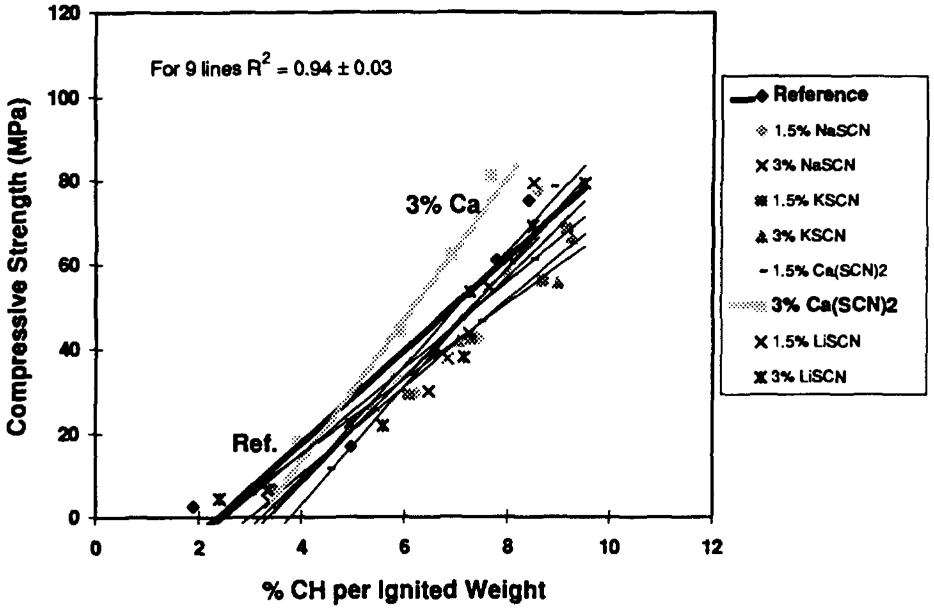

Fig. 7. Relationship between strength and % calcium hydroxide in cement paste hydrated at 0°C.

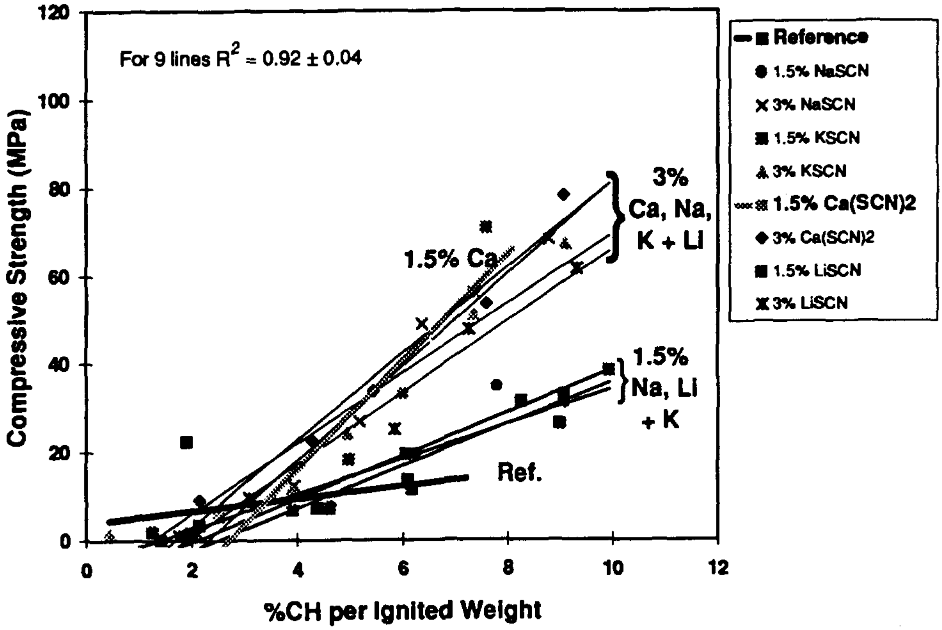

Fig. 8. Relationship between strength and calcium hydroxide in cement paste hydrated at −5°C.

reflected in the conduction calorimetric curves. 1.5% $Ca(SCN)_2$ sample contains twice as much CH as the reference. After 2 days, thiocyanate samples produced the same or slightly higher amount of lime than the reference. 1.5% NaSCN-containing sample had an increased amount of lime over the first three days of the curing period. After 28 days, paste with thiocyanates cured at 0°C contained about 90% of the amount of lime in the reference paste at room temperature. Only 3% $Ca(SCN)_2$ showed lower amounts.

At −5°C, samples contained 0.5–10% CH. KSCN-treated sample contains less CH than the reference after 1 day. All other thiocyanates increased the degree of hydration. After 2 days, all samples showed twice the amount of lime as the reference. This trend continued for the third day. After 28 days, there was about 1/3 more CH present in cubes with thiocyanates. The heat curves also indicated that the acceleration effect of thiocyanates is much more efficient at −5 than at 20°C.

A linear relationship exists between the amount of lime and strength within a certain range of values (Figs. 6–8). The R^2 value for these lines was in the range 0.92–0.94. At 20°C, the paste with 3% Ca thiocyanate exhibits the best strength of all samples when compared at the same degree of hydration (Fig. 6). The paste containing 1.5% K thiocyanate shows the lowest strength of all the pastes, especially at longer curing periods. At 0°C, at the same degree of hydration, pastes with 3% Ca thiocyanate show better strengths than the others. However, most others have similar or lower strengths than those of the reference. The lines for the pastes cured at −5°C can be broadly divided into three groups (Fig. 8). Pastes containing 1.5% Na, Li and K exhibit better strengths than the reference at lime contents > 3%. Best strengths are obtained with 1.5–3% Ca thiocyanate, and 3% Na, K or Li thiocyanates. These data imply that the differences in microstructure of the pastes are responsible for the variation in the intrinsic strengths of the pastes when compared at the same degree of hydration. It has been shown that the intrinsic strengths of cement pastes containing calcium chloride depend on the dosage of the chloride [13].

4. Conclusions

Thiocyanates accelerate the rate of hydration of portland cement cured at temperatures of 20, 0 and −5°C. At low temperatures, this acceleration leads to an increase in the strength development of the paste. A dosage of 1.5% NaSCN or KSCN and 3% $Ca(SCN)_2$ or LiSCN inhibited freezing of water in the pores.

The addition of $Ca(SCN)_2$ to cement paste cured at room temperature results in strengths that equal or exceed the strength of cement paste with no admixture. Addition of $Ca(SCN)_2$ results in the highest rate of heat development and the earliest occurrence of the C_3S peak. The paste with KSCN, although producing the highest heat development after 3 days at room temperature, has strengths as low as 2/3 of the reference value.

Cured at 0°C, pastes with $Ca(SCN)_2$, 1.5% LiSCN, and 1.5% NaSCN exhibit accelerated strength development. These admixtures also release more heat than the reference after 3 days. KSCN produces higher early strengths than the reference but lower values at later ages.

At −5°C, higher concentrations of thiocyanate are more effective for accelerating strength gain. 3% $Ca(SCN)_2$ provides a slightly higher compressive strength than the other salts, and 3% LiSCN is slightly less effective. The total heat curve for 1.5% $Ca(SCN)_2$ shows that some pore water froze, but this did not seem to affect the compressive strength. Samples with 1.5% LiSCN and 1.5 and 3% NH_4SCN also showed the freezing effect in the calorimeter. $Ca(SCN)_2$ and 3% NaSCN increase the strength of cement paste with an increase in CH content.

Calcium thiocyanate is the most effective thiocyanate for promoting strength development. The addition of 3% $Ca(SCN)_2$ to paste hydrated at −5°C results in the 28-day compressive strength that is 74% of the strength of the paste cured at room temperature. The least effective salt was potassium thiocyanate, which produces lower strengths at all curing temperatures. Ammonium thiocyanate releases offensive vapor and therefore is not a viable chemical for practical applications.

The comparative strengths of the pastes containing different amounts of thiocyanates are different when compared at the same degree of hydration, suggesting that the intrinsic strength of the reference paste is different from the paste treated with the thiocyanate. The intrinsic strength of a paste also depends on the type of thiocyanate and its dosage.

References

[1] V.S. Ramachandran, Calcium Chloride in Concrete, Applied Science Publishers, London, U.K., 1976, p. 216.

[2] V.S. Ramachandran, Concrete Admixtures Handbook, Noyes Publications, New Jersey, 1984, p. 626.

[3] B.E. Abdelrazig, D.G. Bonner, D.V. Nowell, J.M. Dransfield and P.J. Egan, Effects of Accelerating Admixtures on Cement Hydration, in E. Vazquez (Ed.), Admixtures for Concrete, Chapman and Hall, London, 1990, p. 106.

[4] E. Senbetta and J.M. Scanlon, Effects of 3 Innovative Admixtures on Durability of Concrete, II CANMET/ACI International Conference on Durability of Concrete, Montreal, Canada, 1991, p. 29.

[5] K. Rear and D. Chin, Non-chloride accelerating admixtures for early compressive strength, Concr. Int., 12 (1990) 55.

[6] J.W. Brook and R.J. Ryan, A year-round accelerating admixture, Super-plasticizers and Other Chemical Admixtures in Concrete, Proc. Third International Conference, Ottawa, Canada, SP-119, American Concrete Institute, Detroit, 1989. p. 535.

[7] J.W. Brook, D.F. Factor, Kinney and A.K. Sarkar, Cold weather admixture, Conc. Int.: Design and Construction, 10 (1988) 44.

[8] A.A. Jeknavorian, N.S. Berke and D.F. Shen, Performance Evaluation of Set Accelerators for Concrete, American Concrete Institute, SP-148, 1994, pp. 455.

[9] C.K. Nmai and J.M. Corbo, Sodium thiocyanate and corrosion potential of steel in concrete and mortar, Concr. Int., 11 (1989) 59.

[10] C.N. Nmai, M.A. Bury and H. Farzam, Corrosion evaluation of a sodium thiocyanate-based admixture, Concr. Int., 16 (1994) 22.

[11] V.S. Ramachandran, Influence of triethanolamine on the hydration characteristics of tricalcium silicate, J. Appl. Chem. Biotechnol., 22 (1972) 1125.

[12] V.S. Ramachandran, J.J. Beaudoin, S.L. Sarkar and Aimin Xu, Physicochemical and microstructural investigations of the effect of NaOH on the hydration of $3CaO.SiO_2$., Cemento, 90 (1993) 84.

[13] V.S. Ramachandran and R.F. Feldran, II Cemento, 75 (1978) 311.