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PORTLAND CEMENT MANUFACTURE CONTAINING LITHIUM FOR ASR CONTROL

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ABSTRACT

A process and composition for portland cement manufacture has been developed using lithium-bearing ores in the raw feed to the kiln for the purpose of incorporating lithium into the clinker to control ASR. Laboratory work and a short trial at a cement plant indicate that the clinkering process can be achieved with lower energy costs per ton of portland cement produced. Analysis of the laboratory produced materials as well as the plant produced materials by x-ray diffraction, optical microscopy, and other means are discussed, as well as mortar bar studies of cement produced in the trial.

Keywords: Alkali-silica reaction, lithium, lithium ore, spodumene, portland cement

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INTRODUCTION

Various forms of lithium, mostly in the form of simple salts, have been shown to be very effective in suppressing expansion from alkali-silica reactions (ASR) (Blackwell et al. 1997, Lumley 1997, Sakaguchi et al.1989, Stark et al.1993). One work describes producing portland cement with lithium hydroxide monohydrate added at the grinding stage to make a portland cement resistant to deleterious expansion (Gajda 1996). However, producing a portland cement with sufficient lithium content to prevent expansions from ASR by adding a refined salt at the grinding stage misses two important advantages compared to incorporating the lithium in ore form in the clinker manufacture itself. The first is that the lithium in the ore form is a less expensive form of lithium, and the other is that lithium ores (and compounds) will act as fluxes during the clinkering operation to either lower the clinkering temperatures.

This paper describes both a laboratory investigation into producing portland cement clinker incorporating lithium ores as well as some results from a brief trial run at a portland cement plant where the lithium-bearing portland cement was produced. In the laboratory study, clinkers were produced using spodumene ore and lithium carbonate. In the trial at the cement plant, only spodumene was used. Spodumene is a lithium aluminum silicate mineral, that, until fairly recently, was the main source for most of the world's production of lithium compounds.

PRELIMINARY LABORATORY STUDIES

This laboratory scale investigation aimed at studying the effect of lithium addition on the phase composition and hydration characteristics of cement clinker. Some work with lithium chloride as a mineralizer (Packter and Zaidi 1976) and of lithium carbonate as intensifier has been reported (Semenov and Zabolotskii 1962, Mathur et al. 1992). Lithium carbonate acts as an intensifier and lowers the decomposition temperature of calcium carbonate and brings down the final clinkering temperature. Test results indicated that lithium decreased the clinkering temperature without affecting the minerals formation, and the resulting cement showed normal hydration characteristics.

Two lithium containing materials were used, spodumene ore with mineral composition: 5.2% Li₂0, 59.5% SiO₂, 5.8% Al₂O, 66.3% CaO, 3.5% Fe₂O₃, 0.7% MgO, 1.7% K₂O, and lithium carbonate. Two clinker mixtures were used, a) raw meal with mineral composition: 21.7% SiO₂, 24.1% Al₂O₃, 2.3% CaO, 2.3% Fe₂O₃, 3.0% MgO, 0.5% K₂O, and b) laboratory prepared mixture. The clinker mixtures studied were composed of either raw meal incorporating 0.00, 0.51, and 0.75% Li₂O (Table 1) or laboratory formulated mixtures containing 0.00, 0.75, and 1.50% Li₂O (Table 2). The mixtures made with the raw meal were adjusted to typical clinker formulation using silica (quartz), calcium carbonate, magnesium carbonate, and sodium carbonate.

The ingredients were thoroughly mixed using water and ceramic binder then ball milled over night, shaped into tablets and burned over foils of platinum. Several burning schemes were used as follows:

- Raw meal was fired at 1400°C for 4 hours.
- Samples containing raw meal and spodumene were fired at 1400°C, 1300°C, and 1200°C for 4 hours.
- · Samples containing raw meal and lithium carbonate were fired at 1400°C for 4 hours.
- Laboratory prepared clinker formulae were fired at 1400°C for 2 and 4 hours; at 1325°C for 4 hours; and at 1200°C for 4 hours.
- Laboratory prepared C₃S and C₂S formulae were fired at 1400°C for 4 hours.

	Reference	Ι	II	III	IV
SiO ₂	21.74	21.29	21.29	21.29	20.95
Al ₂ O ₃	5.75	5.56	5.61	5.76	5.67
CaO	66.33	66.34	66.55	66.44	65.37
Fe ₂ O ₃	3.48	3.44	3.46	3.54	3.48
MgO	2.96	1.81	1.83	1.81	1.80
Na ₂ Oe	0.52	0.51	0.49	0.50	0.50
Li ₂ O	0.00	0.51	0.75	0.75	1.50
Lime Saturation Factor	0.96	0.96	0.96	0.96	0.96
Silica Modulus	2.35	2.36	2.35	2.29	2.29
Alumina Modulus	1.65	1.61	1.62	1.63	1.63
Free Lime	1.10	0.80	1.10	0.93	1.20
C ₃ S	54.0	57.0	57.9	56.4	56.8
C ₂ S	21.8	18.2	17.5	18.7	20.3
C ₃ A	9.4	8.9	9.0	9.3	9.1
C ₄ AF	10.6	10.5	10.5	10.8	10.6

TABLE 1: Compositions of Formulae Made with Raw Meal

In Table 1, formulae I and II contain 0.51% and 0.75% Li_2O from spodumene. Formulae II and IV contain 0.75% and 1.5% Li_2O from lithium carbonate. The free lime contents are as measured from samples burnt at 1400°C for 4 hours. Similar results were obtained for samples burnt at 1300°C. Samples burnt at 1200°C showed higher free lime values.

After burning, the samples were ground to a fineness of 7000 cm²/g \pm 50 cm²/g (as measured by the Blaine method) and mixed with gypsum which was added as 3% SO₃. Samples were characterized by x-ray diffraction. Isothermal hydration calorimetry studies of the clinkers (after grinding with gypsum) were carried out at 38°C and w/c ratio of 0.75. In order to ensure reproducibility of the results, duplicate samples were prepared from starting materials, burned at the same temperature and the same burning scheme, ground to the same fineness, and calorimetry runs were made. The results show excellent reproducibility. Microscopy was also carried out on various clinker samples before grinding. The free lime content was determined by a boiling mixture of glycerol and ethanol in the presence of a catalyst. The amount of liberated CaO was determined by titration with a standard ammonium acetate solution. The ammonium acetate solution is standardized by using pure calcium hydroxide. The results are reported in Tables 1 and 2 and they represent the average of triplicate measurements.

	Reference	I	II	III	IV
SiO ₂	21.83	21.29	21.63	21.82	21.63
Al ₂ O ₃	5.35	5.34	5.30	5.35	5.30
CaO	66.50	66.22	66.73	66.35	65.73
Fe ₂ O ₃	3.41	3.31	3.39	3.40	3.39
MgO	2.60	2.72	2.70	2.61	2.70
Na ₂ Oe	0.72	0.72	0.72	0.72	0.72
Li ₂ O	0.00	0.76	1.50	0.76	1.50
Lime Saturation Factor	0.95	0.95	0.95	0.95	0.95
Silica Modulus	2.49	2.52	2.49	2.49	2.49
Alumina Modulus	1.57	1.60	1.56	1.57	1.56
Free Lime	1.00	1.20	0.86	0.97	1.04
C ₃ S	55.4	55.0	54.2	55.0	54.3
C ₂ S	21.0	21.2	21.3	21.2	21.2
C ₃ A	8.4	8.4	9.0	8.5	8.4
C ₄ AF	10.4	10.3	10.3	10.2	10.1

TABLE 2: Compositions of Formulae Made with Laboratory Formulated Clinker

In Table 2, as in Table 1, formulae I and II contain 0.51% and 0.75% Li₂O from spodumene. Formulae II and IV contain 0.75% and 1.5% Li₂O from lithium carbonate. The Vickers Hardness test was made on the polished sections and was taken as an approximate measure of the relative grindabilities of the samples. An indentation was made with a diamond tip under a certain load and the diagonal distance was measured under the microscope,

Clinker Formulae Made with Raw Meal

A study of x-ray patterns shows the effect of lithium addition on phase composition of the resulting clinker. Lithium addition reduced the burning temperature of the raw meal, and the samples containing 0.51% Li₂O showed complete conversion to cementitious clinker minerals at 1300°C. Samples burned at 1200°C, however, show mainly β -C₂S plus CaO in the diffractogram as confirmed by the high free lime content (23%) as determined by chemical analysis. In other words, the fact that alite is not stable below 1250°C is not affected by the addition of lithium, and the phase composition remains the same as without lithium. The calorimetry results confirm these observations. Similar results were obtained for raw meal incorporating lithium carbonate. There is no significant change in microhardness as a result of introducing lithium to the clinker prepared from raw meal.

Laboratory Clinker Formulae

The x-ray diffractograms of the laboratory clinker incorporating 0.00%, 0.75% and 1.50% Li₂O from spodumene and burnt at 1400°C for 4 hours are shown in Figure 1.



Fig. 1: X-ray diffractograms of laboratory clinkers made with and without spodumene.

Clearly, the diffractograms show no significant effects or changes due to the inclusion of lithium. The corresponding isothermal heat liberated (with gypsum) at 38°C is shown in Figure 2. It is clear that in samples containing lithium, the main hydration peak occurs at earlier time, indicating increase in hydraulic reactivity. Similar results were obtained with samples burnt for 2 hours and with samples incorporating lithium carbonate as well as laboratory clinkers burnt at 1325°C for 4 hours. There is no appreciable change in grindability as a result of lithium addition.

The laboratory synthesized clinker formulae prepared at 1200°C were found to be relatively unreactive with respect to the major cement hydration peaks. The x-ray diffraction pattern shows the presence of large amount of lime and belite indicating very little or no transformation to alite. This result was confirmed by the high free lime content determined by chemical analysis.



Fig. 2: Calorimetry results of laboratory clinkers showing increased hydraulic reactivity with inclusion of lithium. Samples were run at 38°C.

RESULTS FROM THE CEMENT PLANT TRIAL

A trial run at a cement mill made portland cement clinker utilizing two levels of spodumene designed to yield a portland cement with nominal Li₂O contents of 0.17% and 0.34%. The run at the lower level ran for 12 hours and the higher level, 4 hours. While these were very short duration, nonetheless, many important things were observed. Most of the lithium remained in the clinker and was not volatized into the kiln dust, as some had feared. The clinker could be formed at 1250°C with the free lime content only 0.2% to 0.4%. However, contrary to indications in the earlier laboratory study, the C₃S levels, at least by Bogue calculations, were significantly lower in the lithium clinkers produced. Three reasons were suggested for this by the plant personnel. One, that the kiln had never reached equilibrium after changing from one mix to another and was still in transition during the test time, or the mix designs in the raw feed were in error, or that there was either a buildup or sloughing off on the inside of the kiln. It was generally agreed that the test run was too short to resolve this issue at this time, and a longer test would be necessary to more fully answer the above hypotheses. Table 3 gives the compositions of the feed for the lower lithium level, as well as the baseline from the dust collector, the collector during the run, and the clinker analysis during the run.

	Kiln Feed	Baseline Dust	Dust during Run	Clinker
SiO ₂	12.83	16.11	14.30	22.20
Al ₂ O ₃	3.37	4.27	3.76	5.72
Fe ₂ O ₃	1.63	1.99	1.83	3.24
CaO	43.61	30.04	29.58	65.01
MgO	1.48	1.24	1.15	2.35
SO ₃	0.72	12.70	14.25	0.12
Na ₂ O	0.09	0.99	1.13	0.10
K ₂ O	0.66	14.10	15.30	0.16
TiO ₂	0.15	0.27	0.24	0.26
P_2O_5	0.18	0.22	0.20	0.28
Mn ₂ O ₃	0.11	0.07	0.07	0.16
SrO	0.02	0.03	0.03	0.04
ZnO	0.02	0.65	0.70	0.01
Loss on Ignition	35.43	17.46	17.38	0.39
Li ₂ O	0.18	0.02	0.12	0.17
C ₃ A	-	-	-	9.68
C ₄ AF	-	-	-	9.86
C ₃ S	-	-	-	52.53
C ₂ S	-	-	-	24.02

TABLE 3: Analysis of Feed, Kiln Dust and Clinker for the Lithium Clinker (Nominal 0.17% Li₂O)

From Table 3, note that while there was a ten-fold increase of concentration of Na_2O and a twenty-fold increase in concentration of K_2O in the kiln dust (compared to the kiln feed), the concentration of Li_2O actually decreased by 30% in the kiln dust, showing that the majority of the Li_2O remained in the clinker.

Two laboratory cements were produced from the clinkers. One, with the lower lithium level (0.24% Li₂O, in this sample) was made with kiln dust added to increase the total alkali content to 0.83%, and one with the higher lithium level (0.37% Li₂O, in this sample) was made without added alkali and had an alkali content of 0.23%. A normal cement from this plant was also used with an alkali content of 0.31% with the laboratory produced cements in C441 tests. The results are shown in Table 4.

TABLE 4: C441 Results of Normal Cement and Two Laboratory Produced Lithium Cements

	Normal Production (0.31% Na ₂ Oe) (0% Li ₂ O)	Lower Lithium (0.83% Na ₂ Oe) (0.24% Li2O)	Higher Lithium (0.23% Na ₂ Oe) (0.37% Li ₂ O)	
Age	Average Expansion			
14 days	0.012	0.051	0.006	
28 days	0.044	0.081	0.006	
56 days	0.060	0.167	0.009	

A limit of 0.1% at 56 days has been suggested as demonstrating effective levels of ASR control by some researchers (Lane and Ozyildirim 1995). With this criterion, the lower lithium level did not appear sufficient at the alkali content of 0.83%. However, work done by previous researchers indicates that Li:Na molar ratios need to be in the range of 0.74 to be effective (Blackwell et al. 1997). In this laboratory produced cement, the Li:Na molar ratio is 0.60, somewhat below this threshold. However, data in the report suggesting 0.1% at 56 days also show that the expected level for a portland cement at this alkali level would give 56 day expansions in excess of 0.4% (Lane and Ozyildirim 1995). Clearly the Li:Na ratio used here, while not quite sufficient, has greatly suppressed the expansion and is in line with the bulk of the published information on Li:Na ratios necessary, since significant expansion reduction is taking place as the suggested Li:Na levels are approached. The higher lithium content cement, at the alkali level contained, clearly has a large excess of lithium indeed, at 0.23% Na₂Oe, it doesn't need lithium to be considered safe from deleterious ASR. However, significant levels of kiln dust could be recycled back into the cement before it became subject to producing deleterious ASR in concrete due to the lithium content. Also, a high alkali cement could be made with combinations of lithium and pozzolans that could be safe from deleterious ASR expansions.

CONCLUSIONS

The results of the present study lead to important conclusions which can be summarized as follows:

- The overall results suggest the beneficial role of lithium in:
 - · increasing reactivity in the formation of cement clinker;
 - reducing the temperature at which an equivalent degree of reaction may be achieved which represent an additional benefit as energy saving;
 - increasing the hydraulic reactivity of cement formed from a particular clinker composition.
- Spodumene and lithium carbonate decreased the temperature of first melting of the raw meal.
- There was no appreciable effect on the grindability as a result if inclusion of lithium compounds.
- Lithium losses during clinker manufacture from volatization are practically nonexistent.
- Incorporation of lithium into cement manufacture should allow some kiln dust to be recycled back into the portland cement without adding to ASR susceptibility due to the cement's increased alkali content.
- Li:Na ratios shown to be effective by other researchers seem to fit with results shown here, suggesting that there is no additional hydration loss of lithium simply because it is part of the cement itself.

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