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Sorel Cement Reactions and their Kinetics

Terry A. Ring* and Eric Ping[1]
Chemical Engineering, University of Utah, 50 So. Central Campus Drive, MEB 3290, Salt Lake City, UT 84112

Abstract

Mixing solid MgO with $MgCl_2$ brine produces Sorel cement. Experimental cement formulations were developed using ratios of 0.898 to 1.318 kg of MgO per liter (7.5 to 11 pounds of MgO per gallon) of brine with brines that vary in $MgCl_2$ concentration from 20% to 33%. X-ray analysis of the set cement after 24 hours indicates that the dominant setting reaction is:

$$5\ MgO + 1\ MgCl_2 + 13\ H_2O \rightarrow 5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O\ (5\text{-phase})$$

with a significant amount of material that is amorphous in addition to other minor cement components. Cements formulated near the stoichiometry of the 5-phase reaction, e.g. 0.8987 kg/L (7.5 lbs/gal) and 28.9±0.15% $MgCl_2$ brine, are the strongest. Kinetic experiments observed that the 5-phase is formed quickly, but the kinetics are not complete for several days. The cement does not set by the 5-phase reaction when exposed to Cu Kα x-rays but gives a putty like form having $MgCl_2{*}6H_2O$ crystals that do not set into a cement. These are the first observations of x-ray altered cementation reaction kinetics.

Introduction

Sorel cement is produced by mixing a $MgCl_2$ brine solution with MgO powder. Sorel cement is used as fast curing cement for patching the surface of freeways as well as other applications including: stucco, flame retardant coatings and molded cement objects. There is considerable controversy in the literature as to what chemical reaction is responsible for the setting reaction of Sorel cement. In the literature [2,3,4] there are several setting reactions presented. The two most prominent are the formation of a 5-phase hydrated magnesium oxychloride product ($5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$) and a 3-phase hydrated magnesium oxychloride product ($3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$) made by the following reactions:

$$5\ MgO + 1\ MgCl_2 + 13\ H_2O \rightarrow 5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O\ (5\text{-phase})$$

and

$$3\ MgO + 1\ MgCl_2 + 11\ H_2O \rightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O\ (3\text{-phase}).$$

Other setting reactions discussed in the literature[5] include the formation of 2-phase ($2Mg(OH)_2{\cdot}MgCl_2{\cdot}4H_2O$), 9-phase ($9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O$), $Mg(OH)_2$ and

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[1] Present Address: Chemical Engineering Department, Georgia Institute of Technology, Atlanta, Georgia 30332.

[2] Matkovic, B., Popovic, S., Rogic, V., Zunic, T. and Young, J.F., J. Am. Ceramic Soc., 60(11-12) 504-507(1977).

[3] Dehua, D. and Chuanmei, Z., Cement and Concrete Research 29,1365-1371(1999).

[4] Zhang, Z-Y, Dai, C-L, Zhang, Q-H, Guo, B-Z and Liu, W-L., Science in China (Series B), 34(12)1501-1509(1991).

[5] Dehua, D. and Chuanmei, Z., Cement and Concrete Research 29,1365-1371(1999).

$MgCl_2*6H_2O$. In addition to the confusion over the setting reaction, there is a lack of knowledge of the kinetics of the setting reaction and the resulting strength of cements made under different conditions.

This work attempts to first identify which reaction product(s) are observed as a function of the stoichiometry of the mixture, which is adjusted by the ratio of MgO to brine and the brine concentration. Once the reaction products are identified, this work measures the kinetics of the setting reaction using X-ray diffraction analysis. Finally, cement samples with various mixture ratios and brine concentrations are tested for strength. None of the experiments performed use any form of aggregate in the cement mixture, which would tend to increase the strength of the final product.

Experimental Materials

Magnesium oxide: MgO used in these experiments came from two sources. One was an ultra pure analytical reagent grade MgO obtained from Sigma® Chemical Company, St. Louis, MO with a purity of 99.999%. The other was an industrial product, MAGOX 98 HR, obtained from Premier Chemicals, LLC of Bettsville, OH. This material is mined as magnesite ($MgCO_3$) in Gabbs, NV and calcined to MgO. A typical chemical analysis for this industrial product is.

Chemical Composition of MAGOX 98 HR [6]

MgO	85.6% wgt.
CaO	2.7%
SiO_2	2.1%
LOI (H_2O)	4.5%
Fe_2O_3	0.6%
Al_2O_3	0.5%
SO_3	4.0%

The calcium oxide in this material is combined with the free silica as calcium silicate.

$MgCl_2$ brine: Magnesium chloride brine used in these experiments came from two sources. One "pure" brine was prepared from DI water and analytical reagent grade $MgCl_2*6H_2O$ crystals with a purity of 99.99% produced by Mallinckrodt Chemical Company, Paris, KY. And the other "impure" brine was obtained from Great Salt Lake Minerals & Chemical Company, (GSLM) Salt Lake City, UT as a by-product of mineral extraction from the Great Salt Lake in Utah. This industrial brine had the following manufacturing specifications.

Chemical Composition of GSLM Brine[7]

$MgCl_2$	30.00 to 34.00 %wgt.
Sulfate (SO_4^{-2})	0.0 to 3.5%
Potassium (K)	0.0 to 0.7%
Sodium (Na)	0.0 to 0.7%
Water	The balance

[6] Product Literature on MAGOX 98 HR, Premier Chemicals, LLC of Bettsville, OH.

[7] Product specification sheet Great Salt Lake Minerals & Chemical Company, Salt Lake City, UT

Water: Water used for dilution of the GSLM brine and for constitution of "pure" brine and any subsequent dilution was deionized to a conductivity of 18.2 MΩ*cm and filtered to 0.22 microns in a Milli-Q water system[8].

X-ray Standards: For various x-ray standards we used MgO, $Mg(OH)_2$, $MgCl_2*6H_2O$ of analytical reagent grade.

Experimental Methods

Scanning Electron Microscope (SEM) Analysis: Cured cement samples were imaged using a Hitachi S-3000N with energy dispersive x-ray analysis (EDAX) [9]. The cement sample was crushed and a small piece of cement was fixed with carbon tape to the aluminum SEM sample stub. The sample was coated with gold using an RF sputtering apparatus. SEM images were then taken of the cement. In addition, the Premium Chemical Company MgO powder was imaged in the same way and an EDAX analysis was performed on this industrial MgO powder. The EDAX analysis gives the largest impurities as SiO_2, SO_3 and CaO, which is consistent with the manufacturer's chemical analysis, however, this analysis shows slightly more CaO, SiO_2 and SO_3 and less MgO.

Particle Size Distribution: The particle size distribution of the Premium Chemical Company MgO powder was determined using a Beckman Coulter LS230 [10]. A sample of the powder was slurried with DI water using an ultrasonic bath. This sample was further diluted in DI water containing 0.05% sodium metaphosphate in the LS230 to the desired absorbance and analysis performed with the mixing impeller operating at 50%. The sodium metaphosphate is used to colloidally stabilize the particles during the measurement of the particle size distribution. Analysis was performed using a refractive index of 2.24 for the MgO powder [11] and 1.332 for the water [11] at 25±0.5°C. The MgO from Premier Chemical Company has a broad particle size distribution and is heavily aggregated and a broad size distribution with a median size of 16.84 microns.

24 Hour X-ray Analysis: Cements were prepared by mixing a known amount of MgO with a known amount of brine of a particular $MgCl_2$ concentration. A given weight of the MgO powder was placed in a beaker and 20 mL of the brine of a particular $MgCl_2$ concentration was added and then mixed with a spatula for one minute to ensure the mixture was uniformly mixed. The slurry was allowed to set for a 24 hour period. The sample was then crushed and a powdered sample was loaded into a 1.5 cm x 2.0 cm x 0.2 cm holder. X-ray analysis was performed using a PhillipsX'Pert MPD Diffractometer [12]. All XRD scans were performed with Cu Kα radiation, 45mv/40ma, 0.02° step size, and 0.04 sec/step. Peaks were identified by scanning various standards and consulting the JCPDS-ICDD version 1.2 database. In this database the peaks for 2-phase, 3-phase, 5-phase

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[8] Millipore Corporate Headquarters, 290 Concord Rd., Billerica, MA 01821, USA.

[9] Hitachi Instruments Co. Ltd., Yotsuya 4-28-8 Shinjuku-ku, Tokyo 160-0004

[10] Beckman Coulter, Inc., 4300 N. Harbor Boulevard, P.O. Box 3100, Fullerton, CA 92834-3100

[11] Weast, R.C., "CRC Handbook of Chemistry and Physics," 54th edition, CRC Press, Cleveland OH, 1974.

[12] PANalytical B.V. , Lelyweg 1, 7602 EA Almelo , The Netherlands

and 9-phase magnesium oxychloride minerals were given as well as $Mg(OH)_2$ and $MgCl_2*6H_2O$. In addition, the scans performed were analyzed by the PhillipsX'Pert software to identify the various peaks observed in the spectra measured. This software determined the peak heights, backgrounds and peak widths.

Setting Kinetics: Cements were prepared by mixing a known amount of MgO with a known amount of brine of a particular $MgCl_2$ concentration. The cement paste was placed in the x-ray sample holder (1.5 cm x 2 cm x 2 mm thick) and allowed to set at room temperature. At various time intervals, ranging from soon after mixing the paste to 24 hours after mixing, the samples were placed in the x-ray beam for analysis. For each spectrum, a new sample was used so that when a sample was scanned, it had no previous x-ray beam exposure.

Strength Tests: Cements were prepared by mixing a known amount of MgO with a know amount of brine of a particular $MgCl_2$ concentration. The mixed paste was placed in a 5.1 cm diameter cylindrical plastic container and allowed to set for 7 days at room temperature. The sample was then removed from the plastic container. The length of the cement cylinder was 7 cm. Strength tests were performed using a Satec Prism 250 press [13] by applying the pressure axially in compression. Five identical samples were prepared and tested. The pressure at failure for each of the 5 samples was recorded and the average value converted into the compressive stress value at failure and its standard deviation.

$MgCl_2$ concentration: $MgCl_2$ concentration of the brine obtained from Great Salt Lake Minerals & Chemicals Company (GSLM) was measured with an pHoenix [14] chloride specific ion electrode after dilution 1/1000. Calibration standards were prepared with DI water and $MgCl_2*6H_2O$ crystals in the 0.1% to 0.5% $MgCl_2$ range. The calibration curve was linear in this region. The concentration measured for our GSLM brine sample showed a concentration of $33.2 \pm 0.17\%$ $MgCl_2$ by weight.

Brine Density: Brine densities were measured by pyncnometry using a 25 ± 0.02 mL pyncnometer. The pre-weighed pyncnometer was filled with brine and weighed at a temperature of $25 \pm 0.5°C$. The weight of the brine was measured and the density calculated. These measurements determined a density of 1.290 ± 0.003 gm/cm^3 which is also $32.6 \pm 0.26°$ Baume.

Experimental Results and Conclusions

Cement samples were prepared with pure brine and brine from GSLM and MgO from Premier Chemical Company at various brine concentrations and brine to MgO ratios. There were five ratios of MgO to brine used as given in Table 2 and three series of these experiments with different brines A) "impure" GSLM brine at $33.2 \pm 0.17\%$ $MgCl_2$ by weight, B) "impure" GSLM brine diluted to $28.9 \pm 0.15\%$ $MgCl_2$ by weight, C) "pure" brine at $28.9 \pm 0.15\%$ $MgCl_2$ by weight and one experiment with brine D) "impure" brine at $20 \pm 0.11\%$ $MgCl_2$ by weight. For a reference, the mixture of 0.8987 kg MgO/L (7.5 lbs MgO/gal) with 28.9% brine,

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[13] Instron Corporation Headquarters, 100 Royall Street, Canton, MA, 02021, USA

[14] pHoenix Electrode Co., 6103 Glenmont, Huston, Texas 77081

has a slightly higher amount of MgO than a stoichiometric ratio, $MgO:MgCl_2:H_2O$, of 5:1:13 corresponding to the reaction that forms 5-phase. Higher MgO to brine ratios for this brine concentration gives larger amounts of MgO in excess of the 5-phase stoichiometry. The molar ratios for $MgO:MgCl_2:H_2O$ are given in Table 2. Most cements have more MgO than required for the 5-phase reaction. Cements made with 33.2± 0.17% $MgCl_2$ brine and a 0.8987 kg MgO/L (7.5 lb/gal) (MgO to brine ratio) is deficient in MgO and in water. The other ratios in this series of cements, i.e. 0.9586 kg/L (8.0 lb/gal) and higher, have excess MgO in them and are deficient in H_2O for a 5-phase product. These cement mixtures were prepared and allowed to set for 24 hours before x-ray diffraction measurements were made. The x-ray results of these experiments were analyzed and the peak heights associated with specific cementation products are given in Figure 1. As the MgO to brine ratio is increased from 0.8987 kg/L (7.5 lb/gal) to higher values the 5-phase to MgO ratio decreases. The 3-phase to MgO ratio is reasonably constant in Figure 1. The results of cements made with "impure" brine are not drastically different from those shown in Figure 1 using "pure" brine. From Figure 1 we see that the dominant cementation reaction is the reaction that forms 5-phase. Increasing the brine concentration lowers the amount of 5-phase and has little effect on the amount of 3-phase in the cement at 24 hrs. As the brine concentration is lower below 28.9% more $Mg(OH)_2$ is produced with similar amounts of 5-phase and larger amounts of 3-phase but these amounts are still small compared to the 5-phase content. As the brine concentration is raised above 28.9% less 5-phase, more 3-phase and substantially more unreacted MgO is present in the cement at 24 hrs.

Table 1. MgO to Brine Ratios used for XRD and Strength Experiments. All cements contain the Premium Chemical MgO Powder as a source of MgO.

Code	Brine % wgt. $MgCl_2$	lbs/gal	kg/L	Molar Ratio $MgO:MgCl_2:H_2O$
A1	33.2 ± 0.17	7.50	0.89874	4.96:1:10.64
A2	33.2 ± 0.17	8.00	0.95865	5.29:1:10.64
A3	33.2 ± 0.17	9.00	1.07845	5.95:1:10.64
A4	33.2 ± 0.17	10.00	1.1983	6.61:1:10.64
A5	33.2 ± 0.17	11.00	1.3181	7.27:1:10.64
B1	28.9 ± 0.15	7.50	0.89874	5.75:1:13
B2	28.9 ± 0.15	8.00	0.95865	6.13:1:13
B3	28.9 ± 0.15	9.00	1.07845	6.90:1:13
B4	28.9 ± 0.15	10.00	1.1983	7.66:1:13
B5	28.9 ± 0.15	11.00	1.3181	8.43:1:13
C1	28.9 ± 0.15	7.50	0.89874	5.75:1:13
C2	28.9 ± 0.15	8.00	0.95865	6.13:1:13
C3	28.9 ± 0.15	9.00	1.07845	6.90:1:13
C4	28.9 ± 0.15	10.00	1.1983	7.66:1:13
C5	28.9 ± 0.15	11.00	1.3181	8.43:1:13
D5	20 ± 0.11	11.00	1.3181	13.31:1:21.14

Figure 2 shows the compressive strength of series A and B cements after 24 hrs. As MgO to brine ratio is increased cement becomes weaker. The B samples shown corresponds to stoichiometric ratio for 5-phase. It also gives the strongest cement.

Figure 3 shows the x-ray peak height for 5-phase as a function of setting time for cement C1. Here we see the peak height increases drastically in the first 5 minutes then more slowly increases. These results suggest that there is a fast dissolution reaction between the brine and the MgO which slows down as the cement gels and sets. To get this data a series of C1 cement mixtures were mixed and each sample was used for x-ray analysis at a specific reaction time. Should the sample be continuously exposed to x-rays during the curing of the cement, a drastically different cementation process takes place. X-ray exposure during setting yields a putty-like material that has not hardened.

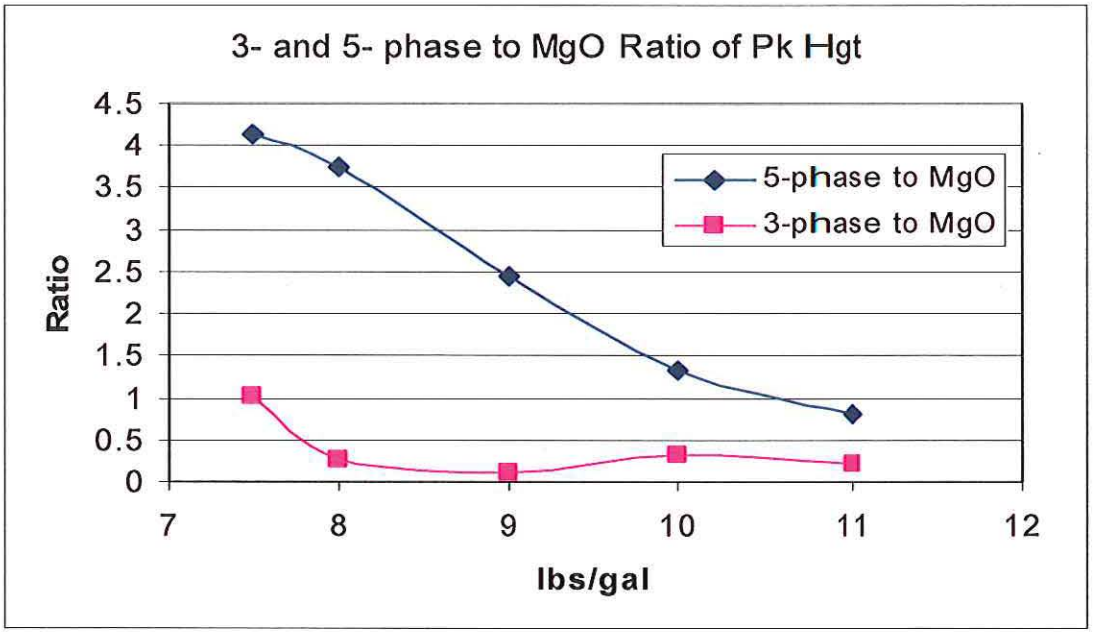

Figure 1. Plot of the ratio of x-ray peak heights corresponding to the 5-phase to MgO ratio and the 3-phase to MgO ratio observed in sample C1 at 24 hour.

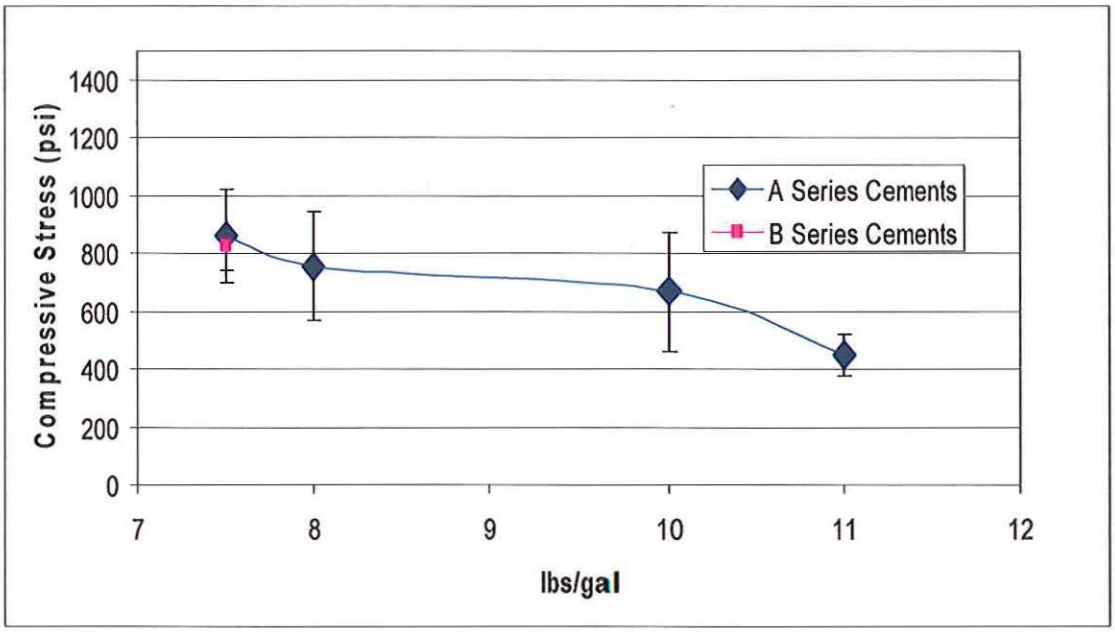

Figure 2. Compressive Strength of Cements as a function of MgO to Brine ratio. These A series cements were made with "impure" 33.2 ± 0.17% wgt $MgCl_2$ by weight brine and the B series cement was made with 'impure" 28.9±0.15% wgt $MgCl_2$. Error bars on the data points correspond to the standard deviation of 5 strength measurements.

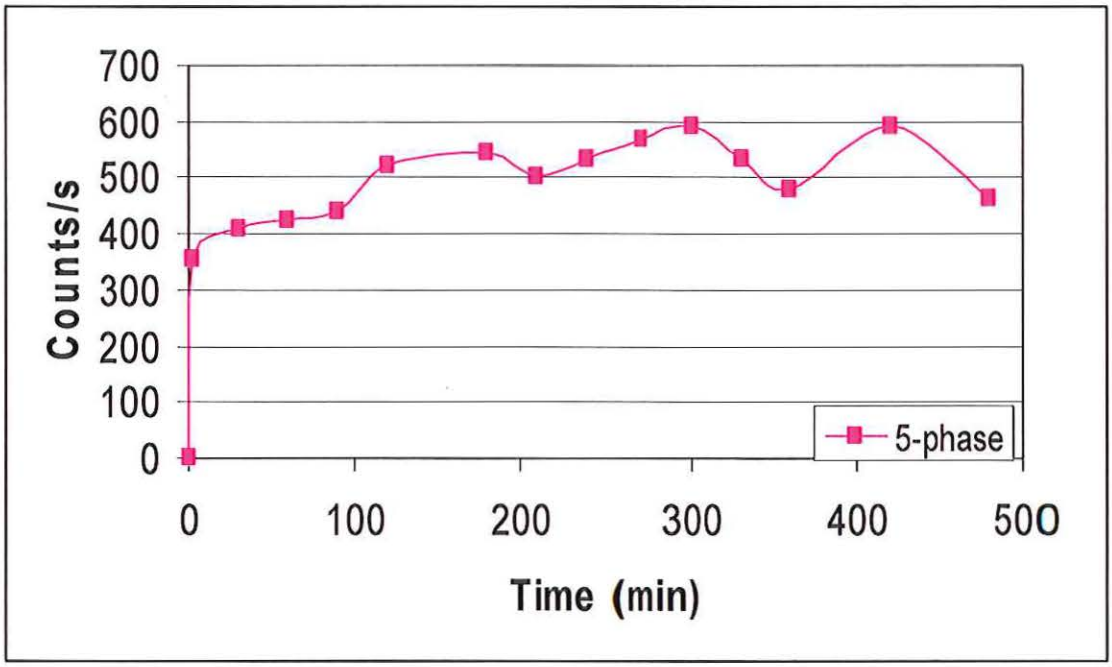

Figure 3. X-ray peak height for 5-phase (2θ= 11.9°) as a function of setting time.

Figure 4 shows the difference between a continuously x-ray exposed and non x-ray exposed sample at 24 hrs. With continuous x-ray exposure the 5-phase material does not form in substantial quantities like it did without x-ray exposure, 3-phase does not form either but the MgO is consumed. The consumed MgO becomes large quantities of $MgCl_2*6H_2O$ in the cement which is not a strong crystal structure leaving an un set putty like mass with x-ray exposure.

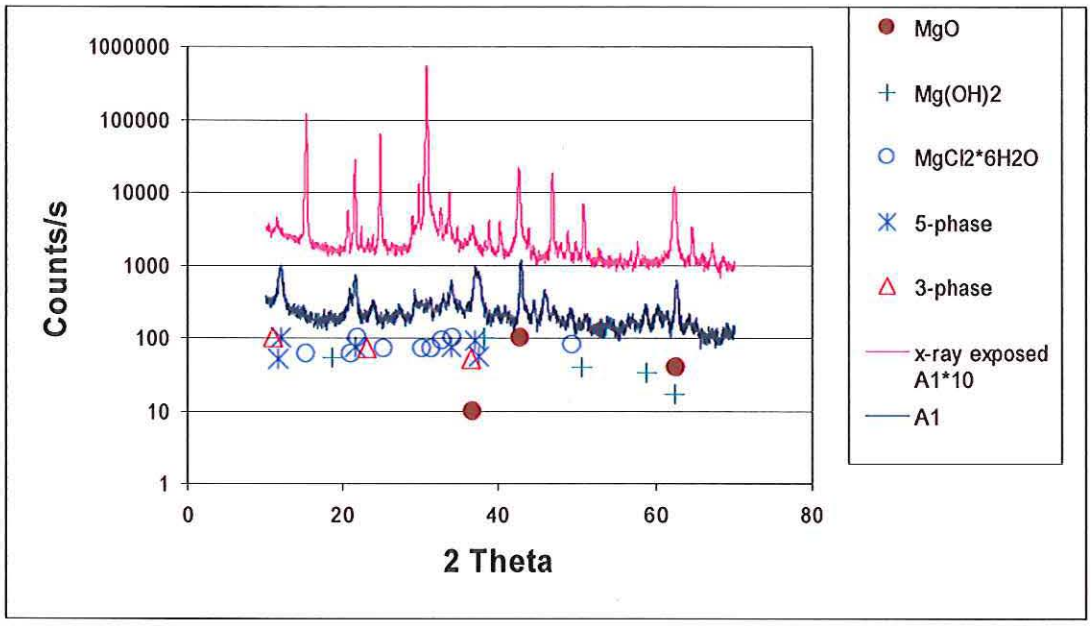

Figure 4. 24 hour x-ray spectra of Cement A1 corresponding to 0.8987 kg "crude" MgO per liter (7.5 lb "crude" MgO per gal) of "impure" 33.2±0.17% $MgCl_2$ brine when sample is exposed to x-rays for 24 Hrs and when it is not exposed to x-rays.

Conclusions

Cements made from MgO and $MgCl_2$ brines set predominately by the reaction:

$$5\ MgO + 1\ MgCl_2 + 13\ H_2O \rightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \text{ (5-phase)}.$$

The setting time is in less than 4 hrs, however, the setting reaction continues for up to 72 hours at an ever-slower rate. After 24 hours of setting, the cements have substantial strengths. Cements with ratios that are stoichiometric with the 5-phase reaction are the strongest observed.

X-ray exposure during setting alters the course of the 5-phase setting reaction giving $MgCl_2*6H_2O$ instead. X-ray expose during setting yields a putty-like material and not hardened cement.