Seventh Symposium on Salt, Vol. I 605–610 (1993)
Elsevier Science Publishers B.V., Amsterdam

Production of Gypsum from Seawater Solar Salt Plants and its Use in the Fabrication of Cements

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ABSTRACT

Gypsum ($CaSO_4 \cdot 2H_2O$) is produced in large quantities as an obligatory by-product from seawater solar salt plants. In these plants seawater is solar concentrated to a density of about 1.220 g/ml in evaporation ponds, further evaporation causes salt to crystallize out; the brine is then fed to the salt crystallizers. Usually, the solar salt process is stopped when the brine density is about 1.250 g/ml.

Investigations conducted in the Araya salt field show that as seawater concentrates to a density of 1.220 g/ml, about 95% of all the calcium present in it crystallizes out as high purity gypsum. In the study it was found that for every 100,000 metric tons of salt produced, about 8600 metric tons of gypsum crystallize out. The field study shows that the gypsum should be harvested every three to four years to maximize the production per unit area of the evaporation ponds, without reducing significantly their brine holding volume.

The laboratory work was conducted in three steps. In the first step, gypsum harvested from the Araya salt field was milled and washed with water. The results reveal that this gypsum is easily washed of all impurities. In the second step, cements were prepared using 95% clinker and 5% gypsum. Gypsum from Araya, Macuro and imported gypsum were tested. The cements were fabricated following the ASTM norms.

In the third step, all the fabricated cements were chemically and physically evaluated. The results reveal that most of the fabricated cements fulfil the specific required values for compressive strength, time of setting, expansion, consistency, and fineness as established by the ASTM norms. The best results were given by the mixture composed of three parts of Araya gypsum and two parts of gypsum from the mines of Macuro.

INTRODUCTION

The production of sodium chloride (common salt) from seawater by natural solar evaporation is an ancient process that has been practised in many areas of the world under a wide variety of conditions. As the world's sources of salt and other minerals become depleted the importance of seawater as a source of various chemicals becomes relevant.

A commonly accepted average composition of Caribbean seawater for seven of the chemical elements present in the highest concentration is tabulated in Table 1 (Basseggio, 1974), and the sequential deposition of the main substances during the progressive solar evaporation is illustrated in Table 2 (Fernández-Lozano, 1966).

High purity gypsum is used in large quantities for the fabrication of special cements. As world sources of this type of gypsum become depleted, new sources must be found. Extensive laboratory experimental work was conducted to determine the possible use of gypsum produced from seawater solar salt plants for the fabrication of cements.

Gypsum: a by-product of seawater salt plants

Gypsum is an obligatory by-product in the natural evaporation process of seawater for the fabrication of salt. Figure 1 reveals that the calcium ion concentration in the brine increases with increasing brine density up to about 1.116 g/ml, then starts to decrease, and when the density reaches about 1.220 g/ml, which is the crystallization point for salt, about 95% of the calcium has precipitated.

Gypsum is being produced commercially in some countries, such as India and Taiwan from solar salt fields. The harvesting is done every two to three years. Extraction is necessary, otherwise the brine-holding volume of the evaporation ponds where the

TABLE 1

Average composition of caribbean seawater (Basseggio, 1974)

Ionic constituents	Concentration (ppm)
Chloride, Cl	28.850
Sodium, Na	11.540
Magnesium, Mg	1.390
Sulphate, SO_4	2.907
Calcium, Ca	0.448
Potassium, K	0.418
Bromine, Br	0.071

TABLE 2

Sequential deposition of minerals from seawater in the natural evaporation process (Fernández-Lozano, 1966)

Brine density (g/ml)	Main solid phases
1.027	Seawater
1.060	Calcium Carbonate
1.162	Gypsum
1.210	Gypsum
1.241	Halite
1.308	Halite + Epsomite
1.321	Halite + Epsomite + Kaenite
1.330	Halite + Kaenite + Carnallite
1.349	Halite + Carnallite + Bischoffite

gypsum crystallizes will be continuously reduced and this will result in a general decrease in the salt production of the system.

It is common practice in seawater solar salt plants to utilize the by-product gypsum as a material for the construction of dikes and ramparts and in the preparation of crystallizer floors. In 1984 an extensive research program was initiated to find industrial applications for this high purity gypsum.

Gypsum as a retarder for the time of setting of cement

Although many theories have been proposed to explain the setting of cements, it is generally agreed that hydration and hydrolysis are involved.

To hold up the "flash set" caused by C_3A (tetracalcium aluminate) some investigators believe that gypsum added as retarder causes the temporary formation of $C_3A{\cdot}3CaSO_4{\cdot}31H_2O$, while others assert that the gypsum gives free $Ca(OH)_2$ by reactions with alkali and, in turn, forms more stable tetracalcium aluminate (Sliepcevich and Katz, 1943; Villegas, 1966).

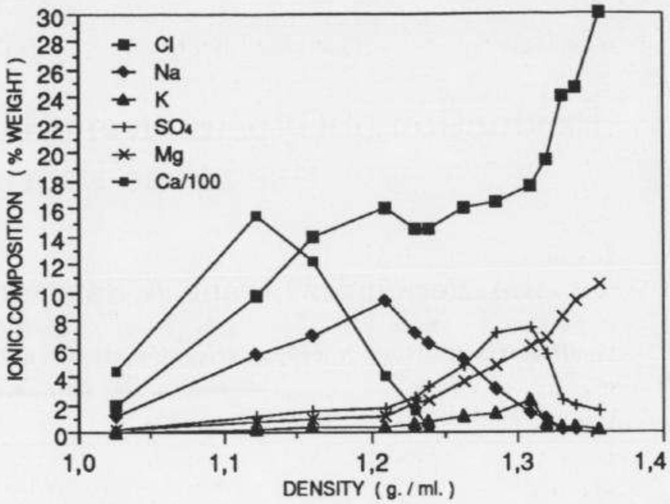

Fig. 1. Ionic composition vs. density of brine for natural evaporation of seawater.

SCOPE OF THE INVESTIGATION

An extensive investigation program was established to achieve the following objectives:

1. Evaluate the conditions for the industrial production of seawater gypsum as by-product from seawater solar salt plants.

2. Evaluate the feasibility of using seawater gypsum as retarder regulator for the setting of cements.

3. Evaluate the chemical and physical properties of the cements prepared with seawater gypsum and gypsum mixtures.

EXPERIMENTAL WORK

Description of the main sets of apparatus

The size reduction units employed were: a jaw crusher, a grinder with discs, a ball mill and a pulverizer.

The apparatus employed for washing the Araya gypsum was designed to accomplish optimum contact between the phases. It consisted of a cylindrical plastic container, with a volumetric capacity of 18 l, and a stirrer system with speed regulator.

The main physical properties of cements measured were: fineness; normal consistency; time of setting; compressive strength; and autoclave expansion.

The values for these parameters are established by ASTM norms; some of these values are tabulated in Table 3. The apparatus used for the tests was that recommended by the ASTM norms.

The chemical composition of the liquid and solid phases was determined by standard volumetric and gravimetric methods. A flame photometer and X-rays powder diffractometer were also used.

TABLE 3

Physical requirements of cements according to ASTM norms

Compressive strength		
Test periods (age):		
3 days	kg/cm^2	70
7 days	kg/cm^2	125
28 days	kg/cm^2	250
Time of setting. Gillmore		
Initial set	min., h.	2
Final set	min., h.	24
Time of setting. Vicat		
Initial set	min., h.	1
Final set	min., h.	8
Autoclave expansion	max., %	1
Normal consistency	min., %	10
Fineness Blain	min., cm^2/g	2800

Raw materials

The reactants used in this investigation were gypsum from a mine in Macuro, Venezuela; gypsum imported from Spain and gypsum obtained as by-product from the salt field of Araya, Venezuela. The seawater gypsum was classified into two different types, according to the brine density at which it was harvested, as follows: gypsum harvested in the density range 1.116–1.220 g/ml and that harvested in the density range 1.162–1.220 g/ml. The composition and other properties of the different types of gypsum and gypsum mixtures are summarized in Tables 4 and 5. It was hoped that the results obtained with gypsum produced at different brine densities would give a good indication of the likely behaviour of seawater gypsum as an additive of cement. The clinker used was produced at a local plant; its composition is given in Table 6.

TABLE 4

Percent gypsum content of the gypsum mixtures added to the clinker for the fabrication of cement

Gypsum mixtures (%)			Brine density during harvesting of gypsum
Number	Macuro	Araya	
1	0	5	1.116–1.220 g/ml
2	1	4	(Unwashed)
3	2	3	
4	3	2	
5	4	1	
6	0	5	1.162–1.220 g/ml
7	1	4	(Unwashed)
8	2	3	
9	3	2	
10	4	1	
11	0	5	1.162–1.220 g/ml
12	1	4	(Washed)
13	2	3	
14	3	2	
15	4	1	

Spain:Macuro gypsum 2:1.

Procedure

Sampling of seawater gypsum

Samples of crystallized gypsum were taken from the evaporation ponds by manually cutting pieces of the hard gypsum crust. These pieces were cleaned of sediments *in situ*, washed with seawater, drained and stored in large containers.

Washing of seawater gypsum

The large gypsum lumps were size-reduced in a jaw crusher to 1, 2 and 3 inches size. A 5 kg sample was placed in the cylindrical tank, water added and the motor of the stirrer switched on at the pre-fixed speed of 250 rpm. After 20 min washing time the

TABLE 5

Average composition of the different gypsum mixtures given in Table 4 (% wt)

Gypsum mixture no.	Purity	$CaSO_4$	SiO_2 +R.I	R_2O_3	CaO	MgO	$CaCO_3$	$MgCO_3$	NaCl	Na_2O	CO_2	SO_3
1–5	89.25	2.47	1.50	0.20	31.85	0.30	3.14	0.63	2.00	0.73	1.38	42.92
6–10	94.13	1.46	2.78	0.06	31.22	0.31	1.87	0.65	2.80	0.82	0.82	43.80
11–15	94.13	1.92	0.45	0.44	31.55	0.15	0.10	0.31	1.73	0.57	0.40	44.80
Spain	92.79	2.50	1.20	0.60	32.81	0.11	2.78	0.23	0.05	–	1.22	44.52
Macuro	57.67	20.81	12.70	0.51	31.94	0.11	8.17	0.23	0.02	–	3.50	39.06

(%) R.I = (%) insolubles; (%) R_2O_3 = (%) Al_2O_3 + (%) Fe_2SO_3.

TABLE 6

Composition of the clinker used in this work

Components (%)	Standard methods (%)	X-ray analyses (%)
SiO_2	22.00	20.74
Al_2O_3	4.11	4.62
Fe_2O_3	4.59	4.83
CaO	66.47	65.59
CaO (Free)	0.45	0.45
MgO	0.43	0.66
K_2O	–	0.42
TiO_2	–	0.27
Total	98.05	96.89

tank was discharged over a sieve, the solid drained, dried at 100°C and stored. Tests were conducted for each gypsum size. The washed gypsum samples were dried and analyzed.

Gypsum from Macuro and Spain

Samples of gypsum from the mines of Macuro, Venezuela, and from Spain were facilitated by C.A. Compania de Cementos (VENCEMOS). The composition of these gypsums and seawater gypsum are given in Table 5.

Cement working mixtures

Sixteen mixtures of cement were prepared of about 10 kg each. These mixtures were 95% clinker and 5% gypsum. The proportions of Araya to Macuro gypsum and Macuro to gypsum from Spain used are tabulated in Table 4.

Before preparing the cement mixtures, the clinker and the gypsum were milled separately. The clinker was first milled in a jaw crusher, and in a second operation it was milled to a final size, so that all passed through sieve number 30. The gypsum was milled in a porcelain mortar until all passed through sieve number 70.

Finally, the cement mixtures were prepared by mixing and milling the clinker and the gypsum, together, in a ball mill to a final fineness Blain of 3800–4000 cm^2/g.

Physical and chemical analysis. The procedures follow for the physical and chemical analysis are that recommended by the ASTM norms.

RESULTS AND DISCUSSION

Gypsum production from seawater

Experiments conducted in the local salt field of Araya enabled the amount of gypsum crystallized out as a function of brine density to be established at industrial level. The results are given in Table 7. These results reveal a total gypsum production of 7 kg per cubic meter of 1.116 g/ml density brine fed to the evaporation ponds. Up to 4.50 kg were produced in the density range of 1.116–1.162 g/ml and 2.50 kg in the density range of 1.162–1.220 g/ml. It was also established that for every 100,000 t sodium chloride produced it is necessary to feed to the evaporation ponds 1.23 million m^3 of 1.116 density brine; this results in the production of about 8600 t of high purity gypsum.

Harvesting and washing of seawater gypsum

The first and most important unit operation in the process is harvesting the gypsum. The harvesting should be carefully done to prevent removal of sediments and other contaminating solids that form the floor of the evaporation ponds. Data on the thickness of the deposited crystalline gypsum layer recorded over a period of several years reveal that extraction should be done every three to four years, as a compromise between maximizing production per unit area, without greatly reducing the brine-holding volume of the evaporators. The evaporation system should be so designed as to permit mechanized

TABLE 7

Amount of gypsum produced from 1 m^3 of 1.116 g/ml density brine as a function of brine density

Density (g/ml)	Amount (kg/m^3)	Accumulative (kg/m^3)	Density (g/ml)	Amount (kg/m^3)	Accumulative (kg/m^3)
1.116–1.125	0.652	0.652	1.162–1.171	0.505	0.505
1.125–1.134	0.965	1.617	1.171–1.180	0.510	1.015
1.134–1.142	1.160	2.777	1.180–1.190	0.385	1.400
1.142–1.152	0.901	3.678	1.190–1.200	0.460	1.860
1.152–1.162	0.822	4.500	1.200–1.220	0.640	2.500

Gypsum produced under natural evaporation conditions

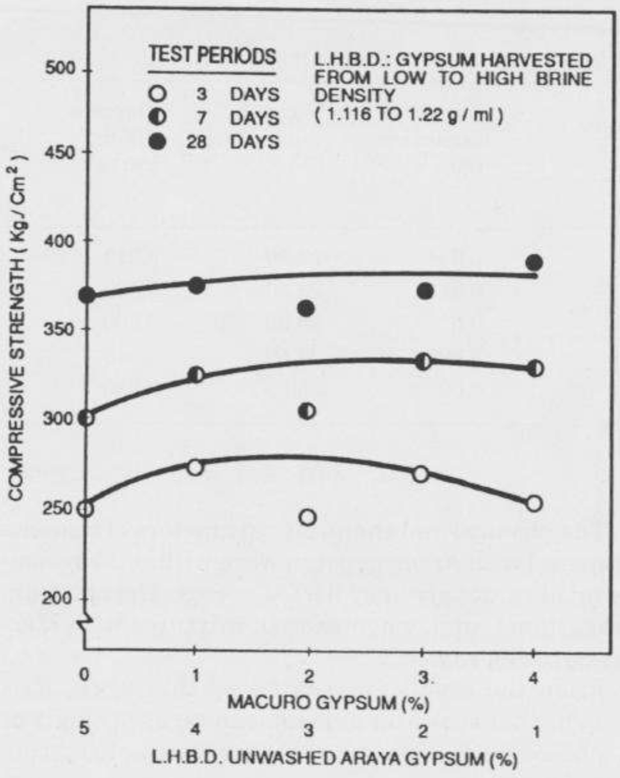

Fig. 2. Compressive strength vs. % Araya unwashed (L.H.B.D.) and Macuro gypsum.

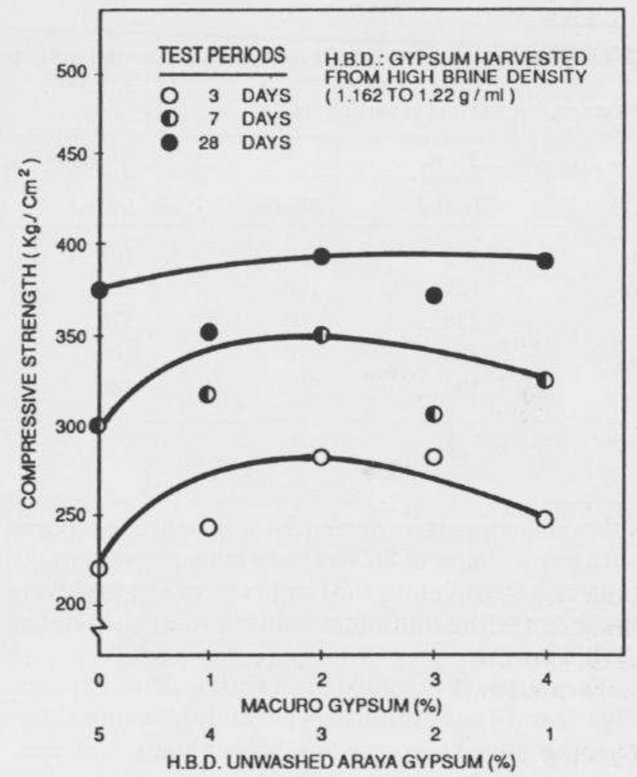

Fig. 3. Compressive strength vs. % Araya unwashed (H.B.D.) and Macuro gypsum.

harvesting without having to stop the flow of brine.

Another important operation is breaking the large pieces of solid gypsum into small lumps; this operation improves the washing of the solids.

A third important unit operation is washing the crystals. This step controls the ultimate product quality. Tests were conducted to establish the feasibility of the removal of brine and other impurities accompanying the extracted gypsum. The results reveal that gypsum is easily washable of impurities.

Gypsum as an additive of cements

The tested gypsums and their mixtures are given in Table 4. The discussion is based mainly on the results obtained for the following parameters: compressive strength, time of setting, autoclave expansion, normal consistency and fineness Blain. These are the parameters most directly affected by gypsum content and purity.

Compressive strength of cements at test periods of 3, 7 and 28 days. Gypsum and gypsum mixtures were intimately mixed with clinker, molded into cubes and the cubes tested according to the ASTM norms.

The values of compressive strength are plotted versus % of Araya and Macuro gypsum in Figs. 2–4.

These plots show the presence of a maximum

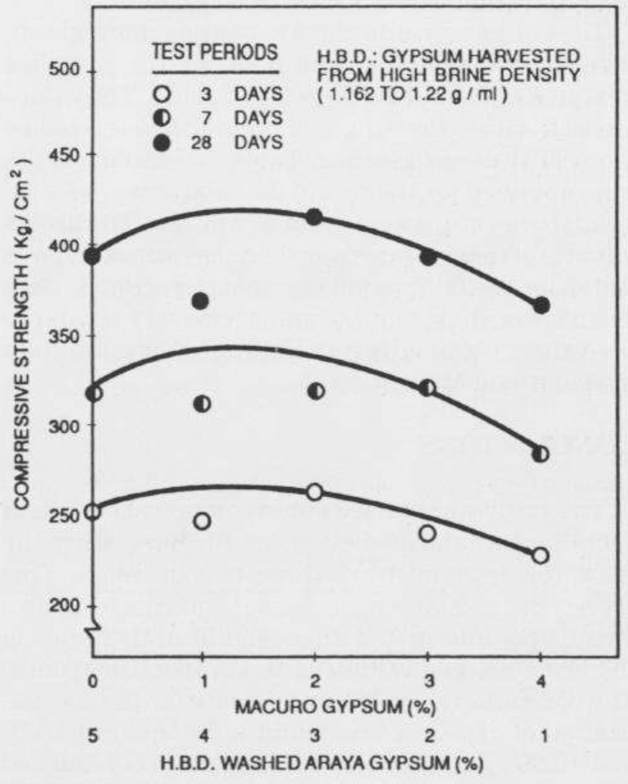

Fig. 4. Compressive strength vs. % Araya washed (H.B.D.) and Macuro gypsum.

TABLE 8

Data for time of setting, autoclave expansion, normal consistency and fineness for the first 5 mixtures of Table 4

Mixture (No.)	Time of setting (min)				Autoclave expansion (%)	Normal consistency (%)	Fineness Blain (cm^2/g)
	Vicat		Gillmore				
	Initial	Final	Initial	Final			
1	130	210	165	205	0.03	23.50	3,912
2	129	190	150	220	0.01	23.50	3,900
3	130	250	175	255	0.03	23.50	3,900
4	130	215	160	250	0.02	23.50	3,940
5	135	255	160	250	0.02	23.50	3,930

value of compressive strength for mixtures prepared with percentages of 3:2 Araya to Macuro gypsum. All the runs show values for compressive strength very much above the minimum values established by the ASTM norms.

For purposes of comparison with washed gypsum, Figs. 3 and 4 were studied separately. A comparative analysis reveals somewhat higher values of compressive strength for runs containing only washed Araya gypsum and for mixtures of 2:3 and 3:2 Macuro:Araya gypsum at the test period of 28 days. Curves for 3 and 7 days show somewhat lower values than that obtained with unwashed gypsum.

Time of setting, autoclave expansion, normal consistency and fineness. The data for the first five mixtures of Table 4 are shown in Table 8. The values are well within the ranges of normal values fixed by the ASTM norms given in Table 3. Similar results were obtained for the rest of the mixtures.

Mixtures of gypsum from Spain and Macuro. A mixture of these two gypsums, in the ratio of 2:1, was tested for the fabrication of cements Portland. Data for this run show that the values are very similar to the values obtained with mixtures of gypsum from seawater and Macuro.

CONCLUSIONS

The study was carried out over a period of several years and established the need for harvesting the seawater gypsum every three to four years. This represents a compromise between maximizing production per unit area without significantly reducing the brine-holding volume of the evaporation ponds. The optimum range of brine density for the crystallization of gypsums was found to be between 1.116 and 1.220 g/ml. The amount of gypsum crystallized out was about 8600 t for every 100,000 t of NaCl produced.

The physical and chemical parameters of cements prepared with Araya gypsum were within the recommended values given by ASTM norms. The optimum proportion found, when used in mixtures with Macuro gypsum, was 3:2.

From the results presented in this work, it is evident that seawater gypsum can be used singly or combined with other gypsums for time-setting control of cements.

Seawater gypsum was found to be easily washable of contaminants, and can be produced with a high degree of purity.

The cements prepared with gypsum mixtures, Araya–Macuro, have similar properties to the cements prepared with gypsum mixtures from Spain–Macuro.

ACKNOWLEDGMENT

We wish to express our thanks to C.A. Venezolana de Cementos (VENCEMOS), Pertigalete-Puerto La Cruz (Venezuela), for their assistance in the performance of the experimental work and to the Empresa Nacional de Salinas, ENSAL, Araya (Venezuela).

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