DESULPHATION OF SEA-BITTERNS FOR ELECTROLYTIC MAGNESIUM METAL PRODUCTION

G N KANNAN, C O AUGUSTIN, S SRIKANTAN, P SUBRAMANIAN, K S SRINIVASAN and P S DESIKAN

Central Electrochemcal Research Institute, Karaikudi-623 006

ABSTRACT

Concentrated sea bitterns obtained from solar evaporation is perhaps the cheapest soure for the production of magnesium metal. The bitterns obtained from different sources have been tested for magnesium metal production. An important step towards the preparation of cell feed from bittern is the desulphation. Since the use of calcium chloride is economically more advantageous for this purpose, the desulphation efficiencies using calcium chloride were studied systematically.

Key words: Sea-bittern, electrolytic magnesium, desulphation

INTRODUCTION

Magnesium metal, in view of its light weight and strength, proves to be a very useful structural material, besides being a strategic metal for use in defence, aircraft, space, metallurgical and electrochemical applications. Magnesium has an inexhaustible source of raw material in sea water. The magnesium content of sea water could be advantageously enriched by solar evaporation in salt pans thus providing a cheap soure of raw material, from which magnesium metal is obtained by electrolysing partly dehydrated magnesium chloride by fused salt electrolysis technique [1].

Sea bittern of 29° Be obtained after the separation of common salt contains several useful substances like bromine and potassium, besides magnesium. The utilisation of bitterns for the recovery of metallic magnesium can hence be done subsequent to the recovery of bromine and potash values.

Salt producing areas in Tamil Nadu and Gujarat in India are climatically suited for obtaining 36° Be bitterns through solar evaporation. For every three tonnes of common salt produced, one tonne of 36° Be bitterns could be produced. The sea bittern of 30° Be has the following composition:

$MgCl_2$	140 gpl
$MgSO_4$	110 gpl
NaCl & KCl	120 gpl

Further evaporation up to 34° Be leads to the separation of most of the sodium and potassium chlorides in the form of carnallite, $KCl.MgCl_2.6H_2O$. Between 34° and 36° Be, the mixed salt is crystallised out. At 36° Be, the bittern is found to contain about 350 gpl of $MgCl_2$, 60-70 gpl of $MgSO_4$ and 40 gpl of NaCl & KCl. This could be favourably utilised for magnesium metal production.

Table I: Composition of bitterns of different density

Constituent	30° Be	34° Be	36° Be
$MgCl_2$, gpl	143.00	280.00	336.00
$MgSO_4$, gpl	108.00	63.00	61.00
NaCl & KCl, gpl	120.00	71.00	26.00
Ratio of $MgCl_2/MgSO_4$	1.32	4.44	5.51
Ratio of $MgCl_2/(NaCl$ & $KCl)$	1.19	3.94	12.92

Even though sea bitterns follow the same composition pattern at various concentrations irrespective of the area in which salt-pans are located, some minor variations in compositions particularly with respect to alkali metal and sulphate content are possible. It is therefore preferable that bitterns from each source is examined, after collecting them at different periods of the season, so that the quantitative flow sheets for different purification steps can be drawn from each case. The bitterns from three different areas of Tamil Nadu coast were examined from this point of view and is presented in Table II.

Table II: Bittern compositions from different locations

Source	°Be	Composition in gpl		
		$MgCl_2$	$MgSO_4$	NaCl&KCl
Tituporur	30	161	69	184
(Chingleput Dist.)	34	269	69	80
	36	375	68	25
Tuticorin	30	153	76	108
(Tirunelveli Dist.)	34	280	73	71
	36	362	68	42
Valinokkam	30	117	86	172
(Ramnad Dist.)	34	269	85	61
	36	355	75	15

DESULPHATION OF BITTERN

Removal of sulphates is the most important purification step for sea bitterns for its use in magnesium metal production. The presence of sulphate in the feed may result not only in the lower yield of magnesium but also causes undesired side reactions resulting in excessive sludge formation, fouling of bath, loss of graphite etc. More than 0.3% of sulphate in the cell feed is not suitable for electrolysis. By eliminating the sulphate suitably, all the magnesium present in the bittern are made available in the form of magnesium chloride for the production of magnesium metal. Studies were hence undertaken to evolve an economic desulphation procedure. The requirements of desulphating agents are: (i) it should be inexpensive and commonly available (ii) the processing steps should not result in further dilution of bitterns (iii) the magnesium value should not be lost during processing (iv) there should not be any fresh contamination of heavy metal and objectionable impurity (v) the pH of the solution should remain neutral (vi) the processing should be preferably done at room temperature and in a single step and (vii) the precipitate obtained should be easily disposable without any pollution problems.
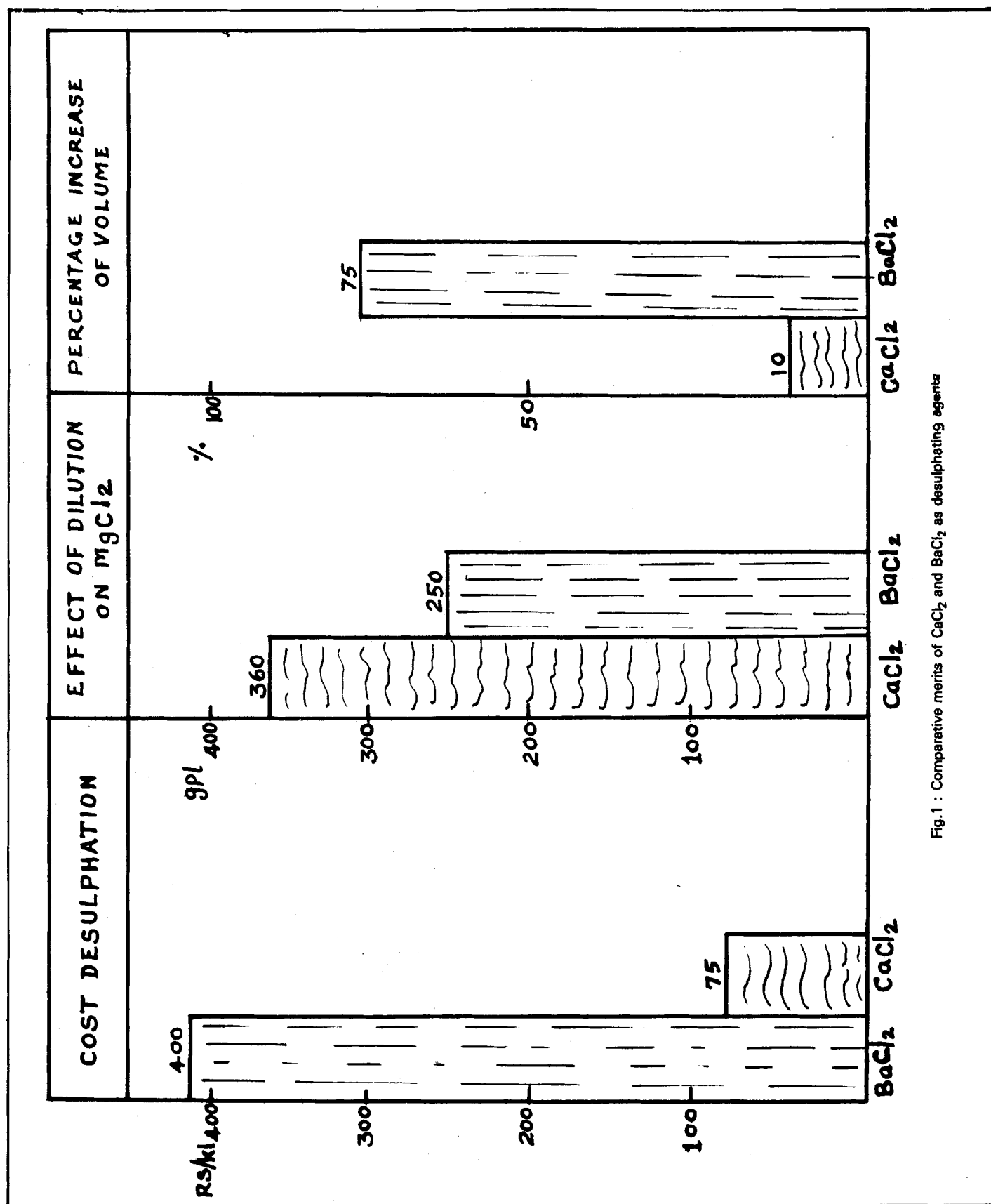
Fig.1 : Comparative merits of $CaCl_2$ and $BaCl_2$ as desulphating agents

The use of barium chloride and calcium chloride as the desulphating agents was studied from the above point of view. While barium chloride is the most effective desulphating chemical under laboratory conditions, it presents several problems in industrial use as listed below:

i) Barium chloride is only sparingly soluble in water and results in the ultimate dilution of the magnesium chloride solution which is not economical for subsequent spray drying purposes.

ii) The cost of barium chloride is very much higher than that of calcium chloride which can be cheaply produced by dissolving powdered limestone in commercial hydrochloric acid.

iii) Because of its higher molecular weight, the quantity of barium chloride for removal of sulphate is nearly double that of calcium chloride.

iv) The barium sulphate effluent, if dumped in the open, is likely to pollute the drinking water in the nearby area, as barium is a harmful impurity for potable and irrigation waters.

It was therefore concluded that calcium chloride should be used as the desulphating agent in commercial scale operation.

Systematic studies of desulphation efficiencies with calcium chloride for different concentrations of sea bitterns were done.

EXPERIMENTAL

Bitterns of different densities were obtained from the actual salt farms. The samples of bitterns were first analysed for all its contents, namely, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-}. Addition of $CaCl_2$ was done in stoichiometric quantities for the reaction.

$$CaCl_2 + MgSO_4 \longrightarrow CaSO_4 + MgCl_2$$
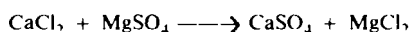
$CaCl_2$ used was prepared by treating lime with commercial hydrochloric acid to obtain about 450 gpl of $CaCl_2$ in solution. The $CaCl_2$ solution in measured quantities were added slowly with constant stirring at room temperature. The precipitation was instantaneous, but the slurry was allowed to settle before filtration. The settling was relatively rapid. The precipitate was filtered and the filtrate was estimated for the SO_4^{2-}. No washing was given to the precipitate in order to avoid dilution of the filtrate. Table III gives the concentration of $MgCl_2$, $MgSO_4$ and (KCl + NaCl) before and after $CaCl_2$ treatment at various densities.

Table III: Desulphation data

°Be	Before CaCl₂			After CaCl₂ treatment		
		SO₄² as			SO₄² as	
	MgCl₂ gpl	MgSO₄ gpl	(NaCl + KCl) gpl	MgCl₂ gpl	MgSO₄ gpl	(NaCl + KCl) gpl
30	117	86	172	156	1.4	147
34	269	85	61	286	0.9	52
36	355	75	15	360	0.5	13

To confirm the results in the pilot plant scale, the treatment of 36° Be bittern (which is the actual raw material for magnesium metal production) was done in 2000 litre batches using rubber lined conical bottomed tanks with stirrers for the reaction and filter press for the removal of precipitate.

RESULTS AND DISCUSSION

Since calcium sulphate, unlike barium sulphate, possesses some amount of solubility, the elimination of sulphate through calcium chloride cannot be total. It has been found that the solubility of calcium sulphate diminishes with higher concentration of magnesium chloride in the solution. Thus, it is found that with solutions of 30-34° Be containing 150 to 280 gpl of magnesium chloride, the sulphate elimination is not complete even with additions of calcium chloride in excess over the stoichiometric requirement.

The elimination of sulphate as insoluble $CaSO_4$ by the addition of $CaCl_2$ solution is based on the principles of solubility product. Precipitate will be formed when the gram ion concentration of the reacting ions in solution exceeds the solubility product constant (K_{sp}) of the sparingly soluble salt. When this happens equilibrium is disturbed and to reinstate equilibrium, excess ions precipitate as non-ionisable solid getting eliminated from the solution (phase), which will continue until the concentration attains values below K_{sp} of precipitate.

For the reacting species of $CaCl_2$, 400 gpl and sulphate, 60 gpl, the total gram ion concentration is 2.25 which is 10,000 times larger than K_{sp} of $CaSO_4$. Hence instantaneous precipitation of $CaSO_4$ occurs. However, a total elimination of sulphate is not rendered possible due to the inherent solubility of $CaSO_4$ which is 1.4 gpl in pure water. This inherent solubility, however, gets lowered in the presence of other salts (in our case $MgCl_2$) and the more the quantity of these other salts the less will be the solubility of $CaSO_4$, (salting-out effort). Thus, desulphated bitterns at 30° Be, 34° Be and 36° Be contain 1.4, 0.9 and 0.5 gpl sulphate as magnesium sulphate respectively (Table III). The decreasing order with increase in concentration can be explained as follows:

(i) 30° Be bittern contains 370 gpl solids and 36° Be bittern contains 478 gpl solids. Considering the solubility of $CaSO_4$ in pure water, the availability of pure water in 36° Be is less than that in 30° Be. Hence reduced solubility and less sulphate.

(ii) It is well known that the solubility is affected by the presence of other salts. More of other salts means less solubility.

(iii) The solubility and K_{sp} of $CaSO_4$, in 36° Be is much smaller than in 30° Be, leading to complete elimination of sulphate by addition of $CaCl_2$ in 36° Be which is not attained in lower° Be bitterns.

The calcium sulphate precipitated in a fine crystalline form is easily filtered off through a filter press or drum filter. The filtrate obtained has the following compositions:

$MgCl_2$	...... 360 gpl
$MgSO_4$	...... 0.5 gpl
NaCl & KCl	.... 13-25 gpl

The NaCl & KCl content is not a harmful impurity since the electrolysis is conducted using a composite bath containing the above salts at much greater concentration. The purified bittern is further processed to get suitable cell feed for magnesium production by molten salt electrolysis.

CONCLUSION

The above studies have led to the conclusion that calcium chloride can be advantageously utilised for the desulphation of 36° Be bittern, one of the primary raw materials for magnesium manufacture, especially when it is produced cheaply reacting lime powder with commercial hydrochloric acid. Added to the cost advantage, the effect of dilution of the bittern is very much avoided when calcium chloride is used instead of barium chloride (Fig.1)

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