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PRODUCTION OF STRONTIUM CARBONATE FROM CELESTITE

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A simple method has been developed to upgrade celestite ore containing 85 % SrSO_4 to 98.5 % by treatment with dilute hydrochloric acid at room temperature. Pilot plant experiments and material balance have been described for the production of strontium carbonate of 98.5 % purity from the upgraded ore by reacting with 12 % sodium carbonate solution for 30 min. at a temperature of 70° using minimum quantities of water.

INTRODUCTION

Mineral celestite which is the main source of strontium salts occurs in Thana Bula Khan, Hyderabad Division, Sind [1]. The ore contains 85% strontium sulphate with a fairly high percentage of an undesirable impurity, viz. calcium carbonate ranging from 7 to 12%.

Strontium compounds which are derived from strontium carbonate have themselves numerous applications in pyrotechnics, fireworks, matches, ceramic glazes and in the purification of caustic soda. At present the ore is used as a filler in the paint industry while strontium salts are imported. With the growth of the concerned industries the demand for strontium chemicals is likely to increase. This work was therefore, undertaken to optimise the conditions for upgrading the ore and for large scale preparation of strontium carbonate of high purity.

A number of methods have been reported in the literature for the conversion of celestite to strontium carbonate. The usual methods are: reduction of the sulphate with coal to sulphide in a reverberatory furnace [2]; by reacting celestite with sodium carbonate at 850° in molten sodium chloride [3]; by grinding celestite with sodium carbonate solution in a ball mill at 60° [4]; by treatment of ground celestite with carbon dioxide and ammonia [5,6] and by reaction with alkali carbonate solution [7,8]. These methods are however, energy intensive and are likely to get limited to small scale preparations unless more economical operations are introduced into them.

In the present work an attempt has been made to modify the process involving treatment with alkali carbonate so as to scale up the laboratory preparation of strontium carbonate from low grade celestite ore to a pilot plant scale.

EXPERIMENTAL

Method. Celestite rock was washed with water to remove the adhering impurities, dried in air and ground to pass 200 mesh sieve. The ground ore was treated with dilute hydrochloric acid (1:4) to remove the carbonates. After settling the acid was decanted. The latter was recycled for further use with necessary adjustment of concentration of the acid. The ore was washed with water, filtered and dried in air. Chemical analysis of the ore etc. was carried out according to standard method [9].

The ore so upgraded was treated with sodium carbonate solution in a beaker and was heated on a temperature controlled hot plate provided with magnetic stirrer. After each run the slurry was filtered with suction and the residue was washed with water until free from sodium sulphate. Sodium sulphate and unreacted sodium carbonate were estimated in the filtrate and the percentage conversion of strontium sulphate was calculated. The parameters for large scale preparation were established on the basis of the values obtained from laboratory experiments.

RESULTS AND DISCUSSION

The celestite rock sample used in these experiments had 85.0% strontium sulphate. After treating the ore with dilute hydrochloric acid, carbonates and a large portion of iron oxide could be removed and the resulting strontium sulphate was upgraded to 98.5%. The chemical analysis of the original ore and upgraded ore are shown in Tables 1 and 2.

Effect of variables on conversion efficiency. Time, temperature, fineness of ore and concentration of soda ash solution are the main variables which affect the con-

version efficiency of strontium sulphate to strontium carbonate and the effect of their variation on the yield of the latter is described below.

Variation of time. For each run, 10 g of upgraded ore was stirred with 6 g sodium carbonate in 50 ml water, maintaining the temperature at 70° and varying the time of reaction from 10 to 50 min. The results are given in Table 2 which shows that the maximum conversion of 94.0% is obtained after 30 min. of stirring.

Variation of temperature. The effect of temperature on conversion has been studied by varying the former from

Table 1. Chemical analysis of celestite ore

	Original ore (%)
Silica and alumina	1.8
Fe ₂ O ₃	0.3
SrO	51.0
SO ₃	37.1
CaO	4.8
CO ₂	5.0
SrSO ₄	85.1 %

Table 2. Analysis of upgraded ore

Silica and alumina	1.38
Fe ₂ O ₃	6.02
SrO	55.70
SO ₃	42.90
CaO	Nil
CO ₂	Nil
SrSO ₄	99.5 %

30 to 90° and taking the reactants in the same proportion as previously while maintaining the reaction time of 30 min. The results in Table 3 show that the maximum conversion is obtained at 70°.

Variation of sodium carbonate concentration. The effect of excess sodium carbonate in a constant volume of solution has been studied by reacting 10 g ore with increasing amount of sodium carbonate in 50 ml water maintaining constant temperature and time of reaction. The results are given in Table 4 which show that 96.6% conversion is obtained when 44% excess sodium carbonate is added. The reaction requires, in equimolar terms, 5.9 g soda ash to react with 10.3 g strontium sulphate. Larger quantities of soda ash would displace the equilibrium to yield higher quantities of strontium carbonate. However, it may be noted from Table 4 that the conversion is only slightly altered on raising the concentration from equimolar to 44% excess.

Variation of fineness. It has been established by the reported data that fineness of ore plays a significant role in the rate of reaction which increases with decreasing size of particles. However, an adequate speed of reaction is obtainable with particles having fineness between 150 and 200-mesh sieve.

In an earlier work [8], the process for the conversion of celestite into strontium carbonate was reported on a laboratory scale. This process is highly energy intensive, since the ore has to be ground to minus 300 mesh, boiled with one normal hydrochloric acid and the final product has to be recrystallized in order to obtain the desired purity.

The optimum conditions for the process as obtained from the above experiments are that the ore should have (a) a fineness between 150 and 200 mesh size, (b) 70° as reaction temperature, (c) 30 min. as reaction time and (d) ore: soda ratio of 5:3 in three times the weight of water.

Pilot plant scale production will be economically highly prohibitive if it has to resort to grinding to less than 300 mesh fineness. Such a low degree of fineness

Table 3. Effect of time on conversion of celestite to SrCO₃

Exp. No.	Upgraded ore (g.)	Na ₂ CO ₃ (g.)	Water (ml.)	Time (min.)	Temperature (°C)	Conversion of SrSO ₄ (%)
1.	10	6	50	10	70	75.5
2.	10	6	50	20	70	88.3
3.	10	6	50	30	70	94.0
4.	10	6	50	40	70	94.2
5.	10	6	50	50	70	94.5

Table 4. Effect of temperature on conversion of celestite to SrCO₃

Exp. No.	Upgraded ore (g.)	Na ₂ CO ₃ (g.)	Water (ml.)	Time (min.)	Temperature (°C)	Conversion of SrSO ₄ (%)
1.	10	6	50	30	30	73.5
2.	10	6	50	30	50	78.2
3.	10	6	50	30	70	94.0
4.	10	6	50	30	90	94.5

speeds up the chemical reaction but it is an expensive operation, since according to this study reactions giving good yield are equally possible with coarser particles of 150 to 200 mesh fineness.

The use of boiling or hot hydrochloric acid needs to be avoided since it corrodes any material of construction. The same results can be obtained by using a slightly higher concentration of the acid which enhances the rate of reaction and dissolves out the calcium carbonate impurities. In the present study the ore is ground to 150-200 mesh fineness and is treated with 3 normal hydrochloric acid at room temperature. The removal of impurities is possible through simple decantation. Temperatures of 70° have been used for large scale reactions since they can be achieved with solar heating also.

Recrystallization has been found superfluous since after treating the ore with dilute hydrochloric acid, carbonates particularly those of calcium and a large portion of iron oxide are removed while the remaining iron is precipitated out, by adding strontium oxide by the common ion effect which enables a 99% purity to be achieved. 12% sodium carbonate solution has been used for carbonation thus avoiding large volumes of aqueous solutions for the reaction.

Pilot plant production. For this study celestite rock was washed with water and dried in the sun whereafter it

was ground to pass 170 mesh sieve. 115 kg of ground ore was treated with 25 kg. of concentrated hydrochloric acid (commercial) in 100 litres of water. Calcium carbonate, strontium carbonate and a major portion of iron oxide was removed. The ore was allowed to settle and washed with water, until free from calcium chloride. The washed ore was then dried in the air. 100 kg. of upgraded celestite ore, 50 kg of soda ash and 500 litres of water were heated in a steam jacketed vessel fitted with a mechanical stirrer for 30 min. The temperature was maintained at 70°. Thereafter the mixture of strontium carbonate, sodium sulphate and unreacted sodium carbonate was removed and transferred to another tank and the clear solution containing sodium sulphate (76 kg) and unreacted sodium carbonate (3 kg) was decanted leaving behind the slurry containing strontium carbonate and unreacted celestite. The slurry was filtered and washed with water.

Crude strontium carbonate was dissolved in dilute hydrochloric acid (120 kg concentrated HCl in 500 litres of water) and the liberated carbon dioxide was allowed to escape. Fe⁺⁺ was oxidised to Fe⁺⁺⁺ by passing chlorine gas in the strontium chloride solution and Fe(OH)₃ was precipitated after neutralizing with strontium oxide. The impurities were allowed to settle and the supernatant strontium chloride solution was decanted. Strontium carbonate was precipitated out from the strontium chloride solution by gradual addition of dilute soda ash solution

Table 5. Effect of excess sodium carbonate on conversion

Exp. No.	Upgraded ore (g.)	Na ₂ CO ₃ (g.)	Water (ml.)	Excess Na ₂ CO ₃ (%)	Time (min.)	Temp. (°C)	Conversion (%)
1.	10	6.0	50	6.4	30	70	94.0
2.	10	6.5	50	15.2	30	70	95.4
3.	10	7.0	50	24.1	30	70	96.0
4.	10	8.1	50	44.0	30	70	96.6

Flow sheet for the production of strontium carbonate from celestite

115 kg (-170 mesh) celestite ore	25 kg		upgrading	
HCl (d. 1.18)	100 kg	→	-----	
water.				
50 kg wash water		→	decantation and filter	→ 190 kg waste
			-----	100 kg upgraded ore
			upgraded celestite	SrSO ₄ - 98.5%
			-----	SiO ₂ - 1.4%
				Fe ₂ O ₃ - 0.1%
60 kg Na ₂ CO ₃			chemical treatment	
500 kg water		→	-----	
50 kg wash water		→	decantation and filter	→ 76 kg sodium sulphate
			-----	3 kg Na ₂ CO ₃ (unreacted)
				550 kg water
				80 kg SrCO ₃ (crude)
				SrCO ₃ - 94.0%
				SrSO ₄ - 4.0%
				SiO ₂ - 1.8%
				Fe ₂ O ₃ - 0.2%
120 kg HCl (d. 1.18)			conversion to chloride	
500 kg water		→	-----	→ 28 kg carbon dioxide
Oxidation and neutralization with Cl ₂			iron precipitation	

			filtration	→ precipitated iron hydroxide

55 kg Na ₂ CO ₃			precipitation	
500 kg water		→	-----	
			decantation and filter	→ 75 kg sodium chloride
			-----	500 kg water
			drying	

			75 kg. strontium carbonate	
			SrCO ₃ - 99.8%	

Celestite ore (-170 mesh)	- 115 kg.		Strontium carbonate	- 75 kg.
Hydrochloric acid (d. 1.18)	- 145 kg.		Sodium sulphate	- 76 kg.
Sodium carbonate	- 115 kg.		Sodium chloride	- 75 kg.
Water	- 1750 kg.		Sodium carbonate	- 3 kg.
			Carbon dioxide	- 28 kg.
			Celestite (unreacted)	- 4 kg.
			Impurities	- 19 kg.
			Water	- 1840 kg.

Total:	2125 kg.		Total:	2125 kg.

(55 kg Na₂CO₃ in 500 litres of water). The precipitated strontium carbonate was allowed to settle and the supernatant solution was decanted. The precipitates were washed with water and filtered by centrifugation. It was then dried on aluminium trays in an oven at 110°. The yield of strontium carbonate was 75 kg containing 99.8% SrCO₃ as per analysis shown in Table 6.

Table 6. Chemical analysis of strontium carbonate (%)

SrCO ₃	99.80
CaO	0.05
Fe ₂ O ₃	0.02
Na ₂ O	0.08
K ₂ O	0.05

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