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Preparation of strontium oxide from celestite:A review

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ABSTRACT

The present work reviews the work of different scientists for the preparation of strontium oxide from celestite by different processes. Celestite being natural ore of strontium is treated to obtain strontium oxide. The study shows that strontium oxide can be prepared by strontium metal powder or by celestite. Strontium oxide is prepared by heating strontium carbonate obtained from celestite with carbon(charcoal) in a resistence-heating furnace at high temperature(1400^{0}C). The conversion consists of multi step preparation. The final product characterization with respect to different analytical tools(physical & chemical) is necessary to get the product of desired level of puritiy. Many processes have been developed to remove the undesired impurities generally associated with the celestite ore by a number of researchers. The preparation of SrO by different methods, its advantage over other processes and utilization of by products are described. The drawback associated with all these processes are for existence of different level of impurities. The removal of impurities requires consumption of lot of chemicals, energy etc. that makes the product costly. In this review article attempt has been made to compare each process by categorizing them specifically. The process developed till date has been compared in terms of utilization of by product environment, energy associated with each process and the most importantly the economical part of the developed process.

INTRODUCTION

Strontium was first detected in the mineral strontianite ($SrCO_3$, named in 1791) found in lead mine at the place Strontian, located on the shores of Loch Sunart, Argyllshire, and Scortland. It appears that it was known since 1764, but could not be recognized at that time. Scrimshank(1787), Crawford(1790), Hope(1791), Klaproth(1793), Kirwan(1794) and Davy(1808) are the names of chemists who were credited for the discovery of strontium. William Cruikshank had done the earliest chemical work in 1787 followed by Irish physician Adair Crawford in 1790. They concluded that it is a new earth material. In 1793 Martin Heinrich Klaproth published a paper describing a series of parallel experiments made with strontianite and witherite (Barium carbonate). In 1794 he prepared strontium oxide and strontium hydroxide. In 1793 Thomas Hoop, Professor of chemistry, Edinburgh University conducted a series of experiments and showed that it contained a “hitherto unknown kind of earth”. He called the mineral strontianite and the new compound was named after the names of mine “Strontia”. During 1807-1808 Sir Humphy Davy managed to isolate the unknown metal strontium from strontianite[1].

Strontium has two minerals, which are found worldwide. The first is celestite($SrSO_4$) and second is strontianite($SrCO_3$). The economic importance of celestite is considerably greater than that of strontianite. Since celestite is abundantly available in most part of world, which is main source of strontium compounds, the extraction of strontium from it has its own importance. Celestite generally occurs in sedimentary rocks such as bedded deposits of gypsum and halite. Celestite ores are obtained by open cast and underground mining. Many important deposits cannot be mined because of unacceptably high level of barium deposit along with specific trace elements [2-5]. The major producers of celestite are Mexico and Spain but largest exporter is Spain. In India celestite is found in Trichirrapalli district and surrounding area of Tamil Nadu. The Indian celestite contains 75-80% strontium sulphate[6].

Between 1870 and 1920 strontianite was the principle starting material for the production of strontium compound. Now it has been completely replaced by celestite due to its wide spread availabilities. Strontium compound like strontium carbonate¸ strontium oxide, strontium nitrate, strontium hydroxide etc. are produced from celestite[7]. Figure 1 shows the application of strontium compound in the different areas. The major uses are television industries, pyrotechnics and ferrite industries respectively. The worldwide production of celestite has been given in figure 2. It appears from the chart that Mexico was the largest producer of celestite during the year 1993-1997 with an increasing order of production. The second largest producer in this period was Spain with a decreasing production in the year 1997. Figure 3 shows the celestite production worldwide during year 2001 to 2006. Spain leads in the production of celestite in this period followed by China.

It is clear from TABLE 2 that strontium carbonate occupies major share as compared to other strontium compounds. Strontium oxide has the lowest demand in comparison to other strontium compound.

Physical properties of celestite

TABLE 1 : General physical property of celestite

Formula	Density g/cm^3	Solubility g/100ml at20^{0}C	Melting point ^{0}C	Crystal structure	Appearance
$SrSO_4$	3.9	0.0113	1580	Orthorhombic	Yellow to faint blue

Crystallography of celestite

Crystal System: Orthorhombic; Class (H-M): *mmm(2lm 2lm 2lm)*- Dipyramidal; Space group: $Pnma(P2_1ln2_1lm2_1la)$; Cell Parameter: a= 8.359 Å, b= 5.352 Å, c= 6.866 Å; Ratio: a :b:c=1.562 : 1 :1.2383; Unit Cell Volume: V 307.17 Å^3(derived from unit cell); Z= 4

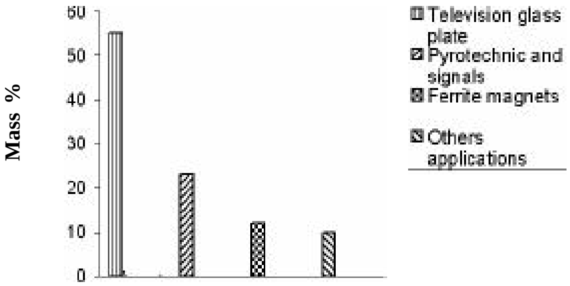

Figure1: Primary application of strontium compound[8]

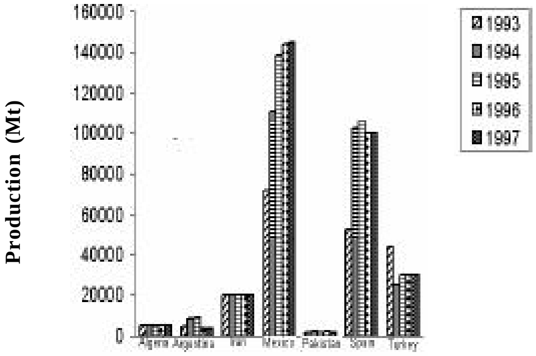

Figure 2 : Worldwide production of celestite (Mt) (year 1993-1997)[8]

TABLE 2 : Total imports by U.S.A from different country qty. in Mt. and values in U.S dollars during year (2004-2005)[9]

Strontium compound	2004		2005	
	Qty. (Mt)	Value US $	Qty. (Mt)	Value US $
Celestite	6290	332000	1820	98400
Strontium carbonate	23600	8430000	1700	6930
Strontiummetal	217	1070000	770	2210000
Strontium nitrate	527	798000	714	637000
Strontium oxide, hydroxide, peroxide	98	75600	8.69	37700

Market trends of strontium compounds

The world-leading producer of strontium carbonate is China. It has the production capacity of 200,000 ton per year. The second and third major producers are Mexico and Germany with plant capacity 127,000 and 70,000 tons per year. China uses mostly its domestic celestite to supply their strontium carbonate producing plants. On the contrary German producers import celestite. The Mexican producers use domestic celestite ore to their plants. The major market for Chinese strontium carbonate is Asia and Europe[10].

The demand for strontium carbonate for television faceplate in glass industries is greater, but appears to be in decreasing trend owing to the growing popularity of flat panel television monitors. During last five years domestic consumption of strontium carbonate in U.S.A has decreased substantially due to closure of television glass plant in U.S.A. China, Europe, and North America are the most important markets for television industries. Southeast Asia and Latin America have higher growth rate potentially representing huge market for television manufacturers and thus strontium carbonate industries[11]. Now-a-days new technology has emerged for preparation of television and computer display such as LCD. This new technology may severally reduce the strontium carbonate demand and at this point strontium producers could experience a major set back. In India the present demand for different strontium compound is around 1500 tones per annum. The demand is largely met by import. The growth rate in demand is approximately 7 to 8%[6].

Application of strontium oxide

Presently strontium oxide is used in frit form below 1100^{0}C. Above this temperature it can be used as a glaze flux. Strontium oxide has been used as substitute for lead oxide in glazes using smaller amounts since it has no toxicity as compared to lead. Strontium oxide develops vivid colors similarly to lead. Strontium oxide when added in small amount improves the high viscous high fire zirconium glazes. The compound SrO exhibits different colours response to copper and cobalt. SrO is slightly more powerful fluxing compound due to its lower expansion. Even though SrO has very high melting temperature it is effective in combination with other fluxes at lower temperature and this gives good example of mixed oxide effect. Strontium oxide is highly thermally stable compound. It finds application in glass, optic and ceramic industries. It is emerging as a promising material for electronic materials and in the production of lightweight structured component for aerospace. In electrochemical application such as fuel cells, it is also being used in glass as sealant. SrO is used for the extraction of strontium metal from electrolysis of its fused salt. The major use of strontium carbonate as strontium oxide is in production of television picture tube glass. It is present in glass at 12-14% on a strontium oxide basis and works as an X- ray absorber[7]. Strontium carbonate is an effective X-ray barrier because strontium has a large atomic radius and its presence is required in the relatively high voltage television sets used in USA and Japan. Strontium carbonate when added to special glasses, glass frits and ceramic glazes, increases the firing range, lowers acid solubility and reduces pin holing phenomenon. Strontium oxide is used to prepare strontium hydroxide, which is used as the source material for the production of strontium peroxide. Permanent ceramic magnets(as strontium ferrite) are another end use for strontium compound. These magnets are used extensively in small direct current motors for automobiles windshield wipers, loudspeakers, magnetically attached decorative items, toys, and other electronic equipment. Strontium compound is used to remove lead impurities during the electrolytic production of Zinc[12-20].

Due to porous nature of strontium oxide it may be used as thermal insulators, automotive catalytic converters, converters, chemical catalysts, heat exchangers[21]. Recently Tsunetake Seki used strontium oxide as catalyst for the Tishchenco reaction of furfural and reported that SrO exhibits high reactivities for the challenging Tishchenco reaction of furfural[22].

Physical properties of SrO

TABLE 3 : General physical property of strontium oxide

Formula	Density g/cm^3	Solubility g/100ml at20^{0}C	Melting point ^{0}C	Boiling point ^{0}C	Crystal structure	Appearance
SrO	5.7	3.8	2530	3000	cubic	White crystalline solid

Chemical properties

Strontium oxide is porous white, hygroscopic powder soluble in water, when exposed to air it forms strontium carbonate. Strontium oxide is used in pyrotechnics, medicine and for preparing strontium hydroxide and pigments. Strontium reacts with hydrogen and forms SrH_2 compound at temperature of 300-400^{0}C. It reacts with H_2O, O_2, N_2, F, S and halogens to produce the expected compounds corresponding to its valence(+2). Strontium and the alkaline earth metal are less active than the alkaline metals but all are strong reducing agents.

Preparations of SrO from different processes

Though SrO can be prepared from Sr metal but the process is not economical. However, for certain applications it is prepared by reacting pure metal, with CO_2. The reaction associated with the process is

$5\ Sr(s) + 2CO_2(g) = SrC(s) + 4\ SrO(s)$

Since the above reaction gives SrO along with SrC it is very difficult to separate SrO from the mixture. Apart from this separation is not economical. Moreover, the starting material is strontium metal powder, which is very expensive[3].

When strontium powder is heated in air at higher temperature strontium oxide(SrO) and strontium nitride(Sr_3N_2) is formed. The reaction involved in this process can be written as;

$2\ Sr(s) + O_2(g) = 2SrO(s)$

$3\ Sr(s) + N_2(g) = Sr_3N_2(s)$

Since separation of SrO from the mixture of strontium oxide and strontium nitride is not easy so its processing is less preferred. This process also requires strontium metal powder, which is costly raw material[3].

From celestite

The conversion of celestite to strontium oxide has been categorized into four categories. According to U.S Bureau of mines report (1959) the most common process to convert celestite to strontium carbonate is soda ash process and calcining process, which is also known as black ash process. As per the report soda ash process is simpler. However, this process gives the product of lower grade. The calcining or black ash method produces strontium carbonate of chemical grade, which has minimum 98% purity, where as soda lime process only produces technical grade strontium carbonate(95% pure). Although the soda ash method is simple process the lower grade product causes it to less preferred method of recovery. The chemical products corporate uses only black ash process for the production of carbonate from celestite[23].

Black ash method

In the year 1972 Pedak et al.[32] conducted the reduction of celestite by using hydrogen and a mixture of hydrogen and carbon monoxide at high temperature. This process has main disadvantage that there is a consumption of large amount of gaseous reductants like H_2, CO etc. Gritis et al. in the year 1985.[25] replaced the gaseous reducing material through solid reducing agent. He performed the experiment with solid reductant i.e. carbon to overcome the excess consumption of reducing gases like CO, H_2 etc. The experiment was done by using celestite and carbon (stoichiometic amount) in a rotary kiln at a temperature of 600°C to 700°C at the loading zone and 1200°C to 1300°C at discharging zone. This process has also the disadvantage of consumption of higher electrical energy since it requires higher temperature. Plewa in the year 1989 studied the kinetics of strontium sulphate with carbon monoxide[26]. Till this date there was no data available regarding kinetics of the reduction reaction of celestite with carbon. In this experiment it was found that water insoluble SrS also forms in considerable amount, which hampers the formation of water soluble SrS. To overcome above mentioned drawbacks Sonawane et al. in the year 2000[27] showed that conversion temperature of celestite into strontium carbonate can be reduced by activated charcoal in presence of some catalyst. Carbon impregnated with various catalysts such as K_2CO_3, Na_2CO_3, $K_2Cr_2O_7$, $NaCr_2O_7$ and lime were investigated in this experiment. The molar ratio of active charcoal with respect to celestite was fixed between 1 to 2.5. He found a substantial decrease in conversion temperature from 1200 to 875°C. The temperature of the conversion reaction was kept 800°C to 875°C with a

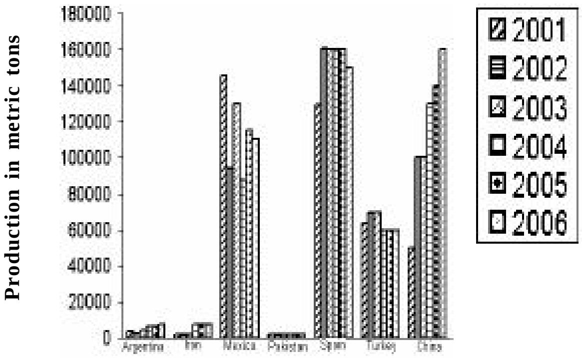

Figure 3 : Worldwide production of celestite (Mt) (year 2001-2006)[9,10]

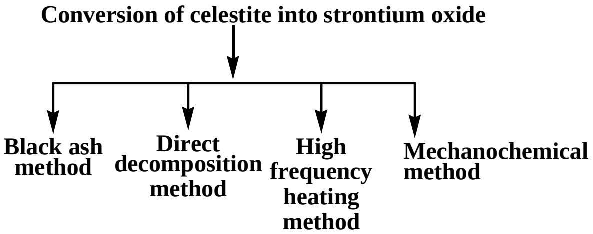

Figure 4 : Flow sheet of different processes for the conversion of celestite to strontium oxide[23-46]

variation of time period from 5 to 90 minutes. Most of the experiments were conducted in inert atmosphere by employing a slow flow of nitrogen gas. The particle size of the celestite and active charcoal was kept less than 105 μm in his experiment. The result indicates that conversion efficiency is better at the mole ratio (charcoal/celestite) 2.5. The extent of conversion increases with temperature from 800^{0}C to 875^{0}C, but there was not much of an increase at 1000^{o}C. The kinetic study shows that there is definite enhancement in the celestite reduction rate when active charcoal with 2% of a catalyst which has been confirmed by Kcat/Knocat values at three common temperature 825^{0}C, 850^{0}C and 875^{0}C. It consists of less time and uses less energy through out the process. This study indicated that lot of time and energy can be saved as the reaction takes place at lower temperature as compared to without catalyst[27]. The formed SrS is then converted to strontium carbonate either by sodium carbonate or ammonium carbonate. The strontium oxide is prepared from the produced styrontium carbonate by heating with carbon at 1400^{0}C[3,7].

Wen Chen in the year 2000[28] studied the reduction of celestite into strontium sulphide and precipitated strontium carbonate from strontium sulphide by Black ash method. The appropriate amount of celestite ore from Lanping was collected for this experiment. The celestite containes approx. $SrSO_4$ 75%, Ba0 0.88%, CaO 1.88%, Al_2O_3 0.46%, MgO 0.6%. Three grades of coals like brown coal, bituminous coal and coke powder were used as reducing agents in this experiment. The appropriate quantity of celestite with coal was mixed properly and heated at 1000^{0}C for three hours. Brown coal was reported as the best reductant. To remove Ba as $BaSO_4$, six to ten times excess of sulphuric acid was added for longer duration of reaction time. The result shows that around 92% of Ba^{+2} was eliminated from $SrCl_2$ solution after 12 hours of reaction time. To remove calcium, magnesium and ferric ions the pH of the solution was increased to 12 to hydrolyze the above ions completely. The strontium carbonate was precipitated by ammonium carbonate by 2 moles/l at a pH 9-11 at temperature 60^{0}C. The strontium carbonate may be used for the preparation of strontium oxide. The figure 5 shows the schematic flow sheet for the production of strontium oxide from celestite.

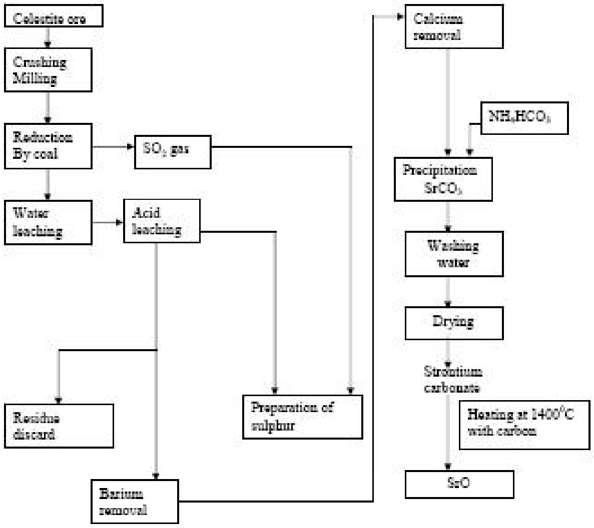

Figure 5 : Schematic flow sheet of production of strontium oxide from celestite by black ash method[28]

Direct decomposition method

In the year 1983 Patent [No. - 4,421,729] describes the process to prepare strontium carbonate from celestite. In this process strontium carbonate was prepared by the reaction of strontium nitrate with CO_2 in aqueous medium. This process has two-stage reaction. The first reaction consists of strontium carbonate precipitation by carbonization with CO_2 in an aqueous solution of strontium nitrate. The second reaction includes neutralization of aqueous nitric acid formed during first reaction. The neutralization is done by addition of lime. Calcium nitrate, a by-product is formed during this reaction. It was claimed that when Ca/Sr ratio is kept within these limit carbon dioxide react with strontium to form strontium carbonate. Calcium carbonate does not form as long as the carbon dioxide is not in excess amount. The desired range of Ca/Sr molar ratio is maintained by adding sufficient amount of lime and nitric acid. The reaction containing precipitation of strontium carbonate and neutralization of nitric acid is conducted at lower temperature less than 50^{0}C preferably between 10^{0}C to 30^{0}C. The controlled mole ratio of Ca/Sr and lower reaction temperature favors the strontium carbonate precipitation and stops the formation of calcium carbonate. Since at lower temperature strontium carbonate is much less soluble than calcium carbonate and therefore precipitation of strontium carbonate occurs.

On the other hand calcium carbonate solubility is increased at lower temperature thus minimizing the chance to co-precipitate calcium carbonate along with strontium carbonate. The pH of the solution medium maintained below 6 more preferably between 4.5 to 6. The pH control of the solution is maintained by adjusting the rate of addition of lime. The lime may be added in the form of CaO or Ca $(OH)_2$ and the lime slurry should contain minimum 5-30% CaO. The reaction time of 25 minutes to 60 minutes is sufficient for the large crystal of strontium carbonate. The obtained strontium carbonate after filtration has been washed to remove any soluble strontium and calcium nitrate. The washed strontium carbonate is dried in oven. The purity of the strontium carbonate reported in this patent is around 90%. To purify further strontium carbonate may be dissolved in hydrochloric acid to form strontium chloride in soluble condition. The filtration of this solution will remove any insoluble residue. The strontium chloride may be precipitated with sodium carbonate/ammonium carbonate solution to give pure strontium carbonate[29]. The dried strontium carbonate may be calcined in an electric furnace at a temperature of 1400^0C for specific time depending on the amount of the sample taken for the preparation of strontium oxide.

In the year 1987 an U.S Patent [No.-4,666,688] claims a novel method for the preparation of strontium carbonate from low and medium grade celestite ore. The process consists of leaching of celestite with mineral acids like HCl, HNO_3 etc. to remove impurities such as Ca, Mg, Ba and iron. After that the residue containing strontium sulphate is treated with ammonium carbonate solution to produce insoluble strontium carbonate. A double decomposition method was employed for getting strontium carbonate of high purity. The difference with earlier processes and this process is the use of ammonium carbonate in place of sodium carbonate. This patent claims that low to medium grade celestite containing up to 80% of strontium sulphate may be converted to strontium carbonate having high purity. The celestite ore is crushed or pulverized in order to provide adequate surface area to complete the reaction (1-50μm). The fine celestite is treated with 10 to 12 % hydrochloric acid. This treatment removes most of the extraneous impurities such as calcium, magnesium, barium and other carbonates by converting them into soluble chloride, which remains in the solution leaving strontium sulphate as insoluble residue. The washed strontium sulphate is treated with ammonium carbonate solution added in slight excess to the stoichiometric value of strontium sulphate present in the celestite ore at a temperature 60-80^0C. The treatment converts strontium sulphate into strontium carbonate. The sulphate present in strontium sulphate is converted to ammonium sulphate as a by-product, which remains in the solution in soluble form. The excess ammonium carbonate solution and the ammonium sulphate is separated from the residue through filtration or by other separation techniques. The strontium carbonate produced in this process is washed with water. This strontium carbonate also contains impurities like silicates, clays and residual iron along with barium compound. In order to extract the strontium carbonate from this residue it is treated with hydrochloric acid (18%) once again. As a result the strontium carbonate dissolves and remains in soluble form as strontium chloride. The solution is filtered to remove the insoluble residue. If the acid solution is contaminated with any impurities like iron or barium, the pH of the solution is increased to 9. The iron hydrolyses which remains insoluble and it may be separated by filtration. In order to remove barium the filtered solution is neutralized with dilute hydrochloric acid. This solution is treated with potassium dichromate to convert the barium into insoluble barium chromate, which can be separated by filteration. The strontium chloride solution free from iron and barium is treated with aqueous solution of ammonium carbonate until precipitation of strontium carbonate occurs. The insoluble carbonate produced is filtered from the solution and washed with water. The produced strontium carbonate in this process contains a purity of more than 99%[30]. The strontium oxide may be prepared from the strontium carbonate by heating with carbon at 1400^0C. The strontium oxide produced from this strontium carbonate will essentially of high purity i.e. 99% or more.

In year 2000 an U.S Patent [No.-6,159,436] has reported in which air/vapor-lift loop reactor is employed to carry out this reaction. This project was examined for carbonate rich celestite ore for the celestite conversion. The acid wash stage is carried out in a mechanically or pneumatically agitated tank with hydrochloric acid. The celestite below 70µm was used for acid leaching. If pneumatically agitation in airlift loop reactor is used, pulps containing up to 60% solids by weight can be easily handled. Under this condition dissolution of carboneous and ferrous gangue, mainly calcite, dolomite, magnetite, and iron oxide along with hydroxide is completed in short period of time. After the acid wash the upgraded concentrate is separated from the solution by sedimentation or by other separation technique. The liquor is transferred to an evaporator for recovering a calcium chloride rich solid. The strontium sulphate enriched concentrate is washed with fresh water before being fed to air/vapour-lift loop reactor for conversion to strontium carbonate using a sodium carbonate aqueous medium. Thus, an almost complete conversion of the strontium sulphate is achieved according to patent claim[31].

In the year 1996 Costillejos E.et al.[33] has conducted experiments for conversion of celestite into strontium carbonate by double decomposition method in aqueous media. The study includes effect of different variables like stirring speed, particle size and concentration of Na_2CO_3 on the reaction rate. In this experiment celestite powder was allowed to react with sodium carbonate in different molar ratio i.e. 1.0, 1.1, 1.2, 1.5 at different temperatures ranging from 25^0C to 75^0C for different time. The complete conversion of strontium carbonate strongly depends on the pH of the solution. The pH of solution should be lower than 9. It also shows that acid leaching with HCl/HNO_3 upgrades the percentage of $SrSO_4$. Experiments were also conducted to find the effect of stirring speed of the solution on the rate of reactions. The observation shows that at stirring speed of 550 rpm there was higher the conversion rate which was independent of intensity of mixing. However, at 150 and 200rpm the reaction rate appeared to be limiting. Effect of particle size of celestite on its conversion shows that with reduced particle size from 275µm to 58µm the rate of conversion of celestite was increased. In this study different processing parameters were optimized to get larger amount of strontium carbonate from celestite. Strontium oxide may be obtained by calcinations of strontium carbonate with carbon obtained from this process at elevated temperature (1400^0C). The flow diagram of the process is shown in figure 6.

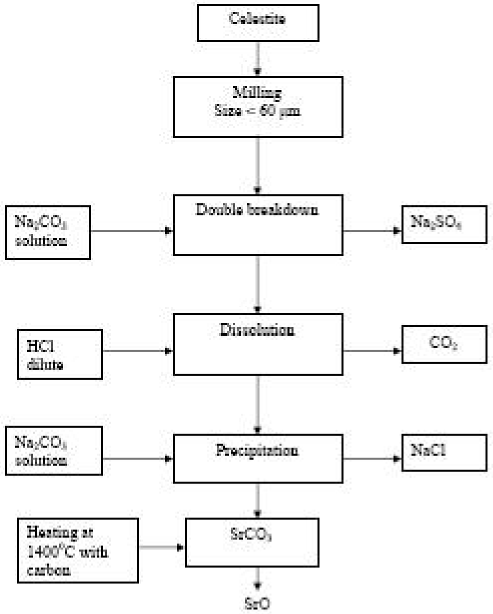

Figure 6 : Schematic flow diagram of double decomposition process for preparation of strontium oxide from celestite[33]

In the year 2004 in another experiment Suarez-Orduna et al.[35]. made another experiment for the conversion of celestite mineral to strontianite under hydrothermal condition. In this experiment a single crystal of celestite was investigated under alkaline hydrothermal condition. Single crystal of mineral celestite was taken from Coahulia, Mexico and was cut parallel to the cleavage(001) direction with 10mm width and 3mm thickness. A celestite crystal approx. 5gm. was placed at the bottom of a Teflon lined stainless steel vessel with inner volume of 27 ml and then the Na_2CO_3 and K_2CO_3 was added to get three different CO_3^{-2}/ SO_4^{-2} ratios(1, 5 and 10) with 17ml of deoxidized water. The conventional hydrothermal treatments were conducted at a temperature($150-250^0$C) by heating the vessel at a rate of 10^0C per minute. The reaction vessel was held at each temperature for several reaction times(1-96h). The cooling stage was maintained by using an electric fan. After the hydrothermal treatment, the reaction products were washed with deionized water in ultrasonic equipment. Strontium carbonate with 99% purity was reported. SrO may be prepared from the strontium carbonate obtained as mentioned above.

In the year 2004 Hacer Dogan et al.[36] studied the effect of acid leaching of Turkish celestite for the conversion of celestite into strontium carbonate. Double

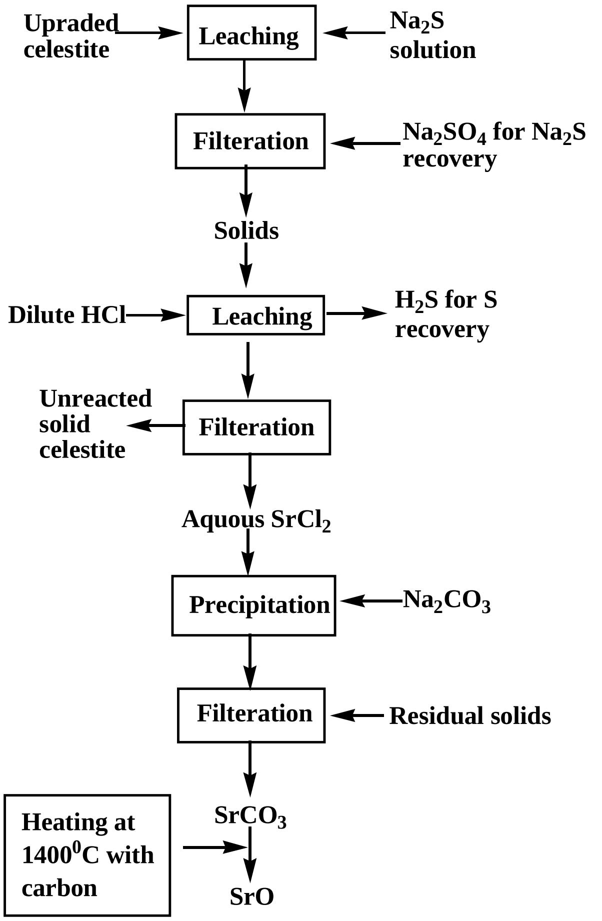

Figure 7 : Shows schematic flow digram for preparation SrO from celestite[37]

decomposition method was employed for conversion of celestite. The impurities associated with celestite were reduced to 0.10g/l by acid leaching. The celestite from Barit Maden, Turkey was taken for this study. Emission spectroscopy with inductively coupled plasma (ICP-AES) was used to verify the Fe, Ca, Pb, Si and Ba contents of the celestite after acid leaching. Different mineral acids like HCl, $HNO_3$and H_2SO_4 were used for acid leaching of celestite. Organic acid such as acetic, oxalic, citric, tartaric and di-glycolic acid was also tested but their price and effectiveness were not as reasonable as inorganic acids. The decrease in calcium percentage was around 0.5% with acid leaching of celestite. Similarly in the case of iron it has reduced reasonably by acid leaching of celestite. Nitric acid, ammonium nitrate and potassium per chlorate were used as oxidizing agent to increase the decomposition of iron. Ammonium fluoride was also used to decompose the silicate material and iron bonded to it. The iron content was lowered to around 0.20g/l with addition of NH_4F. Nitric acid of 3.5% concentration was found sufficient for removal of iron. In this investigation magnetic separation was also employed before acid leaching for removal of very small particle of iron. This step may be effective to avoid large amount of acid consumption in leaching process. This experiment shows that particle size of celestite is very important for the total completion of the reaction. The smaller the particle size of celestite, the lower iron content was obtained under the same condition. The strontium carbonate produced from leached celestite ore contained iron below 0.10 g/l and calcium below 0.2%.

The strontium carbonate found in this process may be used for the production of SrO by calcinations method using carbon as reductant at high temperature as mentioned earlier.

Murat Erdumoglu et al. in the year 2006[37] had carried out the experiment on the leaching of celestite with sodium sulphide at 20^0C in order to prepare strontium disulphide. The acid leaching of strontium disulphide by dilute HCl were conducted to form strontium chloride. Any residue remaining in the strontium chloride solution was filtered and removed. The liquid containing strontium chloride was allowed to react with sodium carbonate solution for the precipitation of strontium carbonate. In this study the reaction kinetics with respect to different parameters like particle size of celestite, concentration of Na_2S, stirring speed was studied. The result showed that the rate of conversion of celestite to strontium disulphide depends on concentration of sodium suphide[40]. The celestite taken in this experiment was upgraded to 99.8% strontium sulphate. Therefore strontium carbonate produced will be of high purity. The strontium oxide of very high purity may be prepared from this strontium carbonate by similar way as described above. The flow sheet diagram of this process is given in figure 7.

Conversion of celestite to SrS by microwave heating[40,41,42]

Most recently in the year 2007 conversion of celestite to SrS by microwave heating was reported by Abdullah Obut[38]. He used charcoal as a reducing agent and heating was done in commercial microwave oven.

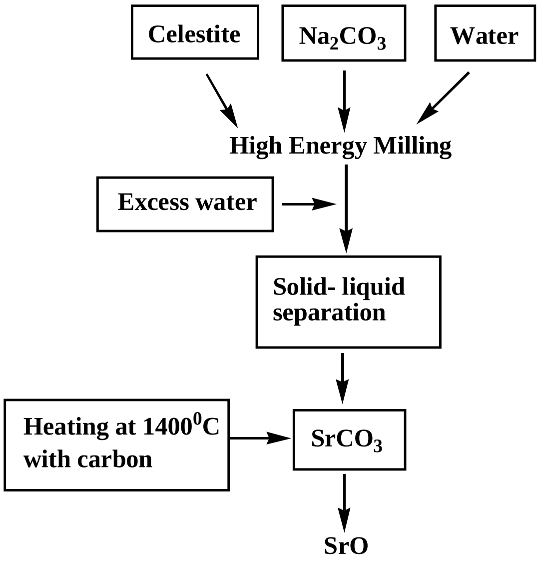

Figure 8 : Schematic flow sheet for the preparation of strontium oxide from celestite by mechanochemical method[43]

In this experiment celestite was taken from Turkey having purity more than 98% particle size less than 200 micron. The laboratory grade charcoal was used. In each experiment appropriate quantity of celestite with stoichiometric, 50% and 100% excess charcoal has been taken and mixed properly. The mixture was heated in a lightly covered porcelain crucible, which is placed inside a commercial microwave oven. The oven was operated at 900W and frequency of 2450MHz for a time of 2,4,7 and 10 minutes. The temperature of the mixture immediately increases by the application of microwave energy due to the strong interaction between microwave and charcoal .The temperature of celestite with stoichiometric carbon reaches 354^{0}C whereas the mixture containing 50% and 100% excess charcoal reaches 880^{0}C in equivalent time. There is no considerable loss in weight until 550^{0}C.The loss values increases steeply after 800^{0}C indicating starting of the reaction. The weight loss value practically stops after 1100^{0}C showing the completion of the reaction. The temperature of stoichiometric ratio reaches 800^{0}C after 7 minutes of microwave heating and after 10 minutes heating its temperature reaches 1160^{0}C. The mixture of 50%and 100% charcoal-celestite exceeds 1200^{0}C.For 50% and 100% excess charcoal–celestite mixture the weight loss values are almost in range with theoretical values indicating complete conversion of celestite to strontium sulphide. The experiment concludes that conversion of celestite to SrS having conversion ratio more than 97% can be achieved through microwave heating. The strontium sulphide obtained by this method may be used for the preparation of strontium carbonate, which can be further used for the synthesis of strontium oxide by above -mentioned process.

Conversion of celestite by mechanochemical method

There is a recent publication in the year 2007 about the conversion of celestite to strontium sulphide. Abdullah Obut et al.[43] made an attempt for the conversion of strontium carbonate from celestite by mechanochemical method. In this experiment(+600µm) Turkish celestite containing 96.12% $SrSO_4$, 2.61%$CaSO_4$, 0.6% $BaSO_4$ and 0.45% Fe_2O_3 has been employed. The reagent grade of sodium carbonate and distilled water was used in this experiment. The planetary type ball mill with 500rpm, ball/sample weight ratio: 20, numbers of balls 50, diameter of balls 10 mm has been used to carry out the mechanochemical reaction. The general flow sheet of the work is given in figure 5. The appropriate quantity of celestite and calculated amount of sodium carbonate along with required quantity of distilled water has been added in the planetary ball mill. After milling calculated amount of distilled water was added to milled mixture to solublize Na_2SO_4 formed. After the milling the solid and the liquid portion were separated by centrifugation. After drying, the solid fractions were leached with dilute HCl.The milling experiments were conducted for 10, 20and 40 minutes in an interval of 10 minutes to prevent temperature rise in planetary ball mill. The result shows that 74.23% of celestite is dissolved in distilled water only after 10 minutes of milling. The dissolved sulphate and dissolution percentage of initial celestite and milled solids increases from 91.52% to 93% for 20 minutes. After 40 minutes of milling 98% celestite dissolved. The dissolved sulphate is strontium carbonate. The result also indicates that the increase in dissolution values of sulphate for 20 and 40 minutes is not as significant as the values between 10 to 20 minutes mixing. The effect of amount of sodium carbonate on the preparation of strontium carbonate was also investigated in this experiment and it was found that 10 minutes milling is preferred over 20 minute milling in relation to reduce tungsten carbide ball milling chamber wear. The result also shows that 1:1.2 mole ratio (strontium sulphate/sodium carbonate) and 20 minutes activation time is sufficient for 90% of conversion celestite into strontium carbonate. The whole experiment concludes that the reaction between celestite and strontium carbonate in aqueous medium is diffusion controlled because of the formation of solid strontium carbonate layer over the celestite particle. Whereas in wet high energy milling gives increased rate of conversion of celestite due to creation of fresh reactive surfaces as a result of continuous mixing and size reduction. The strontium oxide may be prepared by heating the strontium carbonate powder with carbon at 1400^{0}C.The flow diagram is given in figure 8.

Recently in the year 2007 Tanaka Knniaki[47] has prepared strontium oxide thin films as an electron injection layer for organic EL De reactive ionization assisted deposition method. The electrical deposition method, which create an oxide layer of strontium oxide on the surface of strontium metal. It cannot be processed for the preparation of strontium oxide in bulk.

CONCLUSION

Celestite contains a lot of impurities like Ca, Ba, Fe etc. which requires removal before conversion. By studying different papers/patent, it is concluded that celestite is firstly converted to strontium carbonate and then SrO is prepared by heating it at higher temperature. There are mainly two methods employed for the conversion of celestite to strontium carbonate. The first method is black ash method and other is direct conversion method. In Black ash method celestite is heated with carbon to get SrS by which strontium carbonate is formed. Strontium carbonate is obtained directly by reacting with leached celestite. Some researchers preferred Black ash method on the basis of less consumption of acids etc. A group of other researcher has preferred direct ash method since this method doesn't require high temperature. Both methods have its own significance. The by products obtained by direct decomposition method are value added product and may be used in corresponding chemical industries. Strontium oxide is prepared by heating strontium carbonate with carbon at high temperature. In another way heating strontium sulphide at high temperature can also form strontium oxide. Since both the processes require high temperature, strontium oxide may be used as flux agent together with other oxides. Apart from this mechanochemical and microwave heating methods which were introduced recently in this current year for the celestite conversion appears to be most promising methods. But these experiments are on early stage for its commercial use. To start its application in bulk production it needs optimization of various parameters, which are involved in these processes.

This review study indicates that there is need to develop other economical process needs to be established for the commercial production of SrO from celestite. The more research on its applicability on different area of science must be identified.

In India there is large deposit of celestite. To explore the Indian technology for the celestite application for the preparation of different strontium compound needs to be searched. The application of strontium oxide in India along with other countries in new areas needs to be focused to promote the production of strontium oxide to make it material of commercially important. This will help to utilize the large deposit of Indian celestite in better ways particularly in the area of production of strontium compound.

REFERENCES

[1] http://elements.vanderkrogt.net/elem/sr.html
[2] W.Hong; 'Celestite and strontionate', Industrial minerals, 55-59 **(1993)**.
[3] Kirk-Othmer; 'Encyclopedia of Chemical Technology', 4th edition, John Willey & Sons, **10**, 947-955 **(1997)**.
[4] A.Joyce Ober; Strontium from Mineral Commodities Summaries, U.S Bureau of Mines., 1323-1332 **(1992)**.
[5] Strontium ch. in Mineral Facts and Problems, U.S. Bureau of Mines Bulletins, 675 **(1985)**.
[6] www.tidco.com
[7] 'Ullmann's Encyclopedia of Industrial Chemistry', 5th edition, VCH, **A25**, 321-327 **(1994)**.
[8] A.Joyce Ober; USGS Mineral yearbook, 1-6 **(1998)**.
[9] Joyce Ober; USGS Mineral yearbook, 1-7 **(2006)**.
[10] U.S. geological survey, Mineral commodity summaries, 1-2 **(2007)**.

[11] 'Strontium ch. in industrial mineral and rocks', 7th edition, Society for mining, metallurgy and exploration Inc., **(2006)**.

[12] 'Metals Handbook', 9th edition, American Society of metals, Metals Park, OH, **1**, 21 **(1979)**.

[13] C.I.Mantell; 'Strontium' in C.A.Hampel; Rare metal handbook, 2nd edition, Reinhold Pub. Co, London, 27-31 **(1961)**.

[14] 'Strontium- supply, demand and technology', U.S. Bureau of Mines Information Circular 9213 **(1989)**.

[15] S.A.Solvey; Electrolysis–Zinc electrolysis, (http://www.solvey-bariumstrontium.com/market/application/0.0,-_EN-1000126-1000330.00.html. **(2000)**.

[16] W.G.Lidman; Foundry Management and Technology, **112(8)**, 46-47 **(1984)**.

[17] J.A.Conkling; Chemistry of fireworks, Chemical and Engineering News, **59(26)**, 24-32 **(1981)**.

[18] T.H.Haberberger; 'Ferrite Application Ever Changing and Expanding', Ceramic Industry Magazine, **115**, 29-32 **(1971)**.

[19] R.G.Wager; Glass as a CRT Fabrication Material Glass, **63**, 191-192 **(1986)**.

[20] 'Metals Handbook', 9th edition, 'American society of Metals', Metal Park, OH, **2**, **(1979)**.

[21] H.Szelagowski, I.Arvanitidis, S.Seetharaman; Journal of Applied Physics, **85**, 193-198 **(1999)**.

[22] Tsunetake Seki, Kazumasa akatsu, Hideshi Hattori; Chem.Commun, 1000-1001 **(2001)**.

[23] U.S. Beauro of mines-A report, **(1959)**.

[24] I.Arvanitidis, S.C.Du, H.Y.Sohan, S.Seetharaman; Metallurgy and Materials Processing science, **28(6)**, 1063-1068 **(1997)**.

[25] E.B.Gitis, P.I.Stigunov, S.K.Solynaik, L.F.Vasileva, F.D.Pushkanov, Y.N.Zinchencho, V.I. Krasinyakov; Otkritiya Izobret, **46**, 1 **(1985)**.

[26] J.Plewa, J.Steindor, J.Nowakowski; Thermochem Acta, **138(1)**, 55 **(1989)**.

[27] R.S.Sonawane, B.B.kale, S.K.Apte, M.K.Dongare; Metallurgical and Material Transaction, **31B**, 35-41 **(2000)**.

[28] Wen Chen, Yun Zhu; Mineral Processing and Extractive Metallurgy, **109**, 65-68 **(1998)**.

[29] U.S.Patent No-4421729, **(1983)**.

[30] U.S Patent No-4666688, **(1987)**.

[31] U.S Patent No-6159 436. **(2000)**.

[32] E.Pedak, M.Allsalu, M.Kanter; Zh.Prikl.Khim. Leningrad, **45(12)**, 2619-23 **(1972)**(in Russian).

[33] A.H.Castillejos, F.P.De La Cruz Del, B.A.Uribis; Hydrometallurgy, **40**, 207-222 **(1976)**.

[34] J.Griffiths; 'Celestite Industrial Mineral', 21-35 **(1985)**.

[35] R.Suarez-Orduna, J.C.Rendon-Angeles, J.Lopez-Cuevas, K.Yanagisawa; Journal of Physics Condensed Matter, **16**, 1331-1334 **(2004)**.

[36] Hacer Dogan, Murat Koral, Sidika Kocakusak; Hydrometallurgy, **71**, 379-383 **(2004)**.

[37] M.Erdemoglu, M.Canbazoglu, H.Yalcin; Trans.Inst.Min.Metal Sec C-Mineral Processing Extractive Metal, **109**, 65-68 **(1998)**.

[38] Abdullah Obut; Materials Engineering, **(2007)** Article in Press.

[39] M.Iwai, M.Toguri; Hydrometallurgy, **22**, 87-100 **(1989)**.

[40] J.M.Osepchuk; Transaction on Microwave Theory and Techniques, **32(9)**, 1200-1224 **(1984)**.

[41] K.J.Rao B.Vaidyanathan, M.Ganguli, P.A.Rama krishnan; Chemistry of Materials, **11**, 882-885 **(1999)**.

[42] D.E.Clark, D.C.Folz, J.K.West; Material Science and Energy, **A287**, 153-158 **(2000)**.

[43] Abdullah Obut, Peter Ballaj, Ismail Girgin; Mineral Engineering, **19**, 1185-1190 **(2006)**.

[44] K.A.Kobe, N.J.Deiglameier; Ind.Eng.Chemistry, **40**, 1988-1990 **(1946)**.

[45] Q.Zhang, F.Saito; Chemical Engineering Journal, 79-82 **(1966)**.

[46] S.W.Kingman, N.A.Rowson; Minerals Engineering, **11**, 1081-1087 **(1998)**.

[47] Tannaka Kinkai, Usai Hiroaki; IEIC Technical Report, **99**, 25-30 **(1999)**.