



Coupled process of reaction and solvent extraction[☆]

I. The reaction between CO₂ and SrCl₂ coupled with solvent extraction of HCl

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Abstract

In order to ensure the continual reaction between CO₂ and SrCl₂ to produce SrCO₃, it is necessary to neutralize produced HCl or to remove it to another phase. Coupling the reaction with solvent extraction is a way to lower the acidity of the aqueous solution and to allow the reaction to proceed continually. Based on this coupled process, a new flow sheet for producing strontium carbonate from celestite is proposed. The factors influencing equilibrium of the coupled process of strontium carbonate production with solvent extraction have been studied.

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1. Introduction

While the production of strontium compounds from celestite was known in the 19th century, it took the discovery that strontium could be used as a safety X-ray absorbent in television screen glass to greatly accelerate production. Screen glass now represents 70–90% of the total production of strontium compounds. They are also widely used in magnetic,

coating, plastics, medicine and pesticide products. In China, the production of strontium carbonate has increased more than 10-fold during the last 20 years.

1.1. Processes for production of strontium carbonate from celestite

The most important strontium mineral is celestite (SrSO₄). Digestion of celestite is usually achieved by high-temperature reduction or double decomposition in solution.

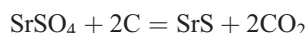
The reduction process involves reacting the ore powder with solid reductants (such as coal and coke) or gaseous reductants (such as natural gas and water

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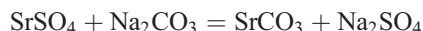
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gas) at 1000–1200 °C to reduce sulfate into sulfide and polysulfide. The main reaction is as follows:



Because the final product strontium sulfide exhibits a dark color, this is known as the “black ash process,” which was first introduced by Terns in 1920 (Joyce, 1989). The black ash is then leached with hot water to dissolve SrS and SrS_n, which partly hydrolyzes as SrHS and Sr(OH)₂ in solution. Sparging CO₂ or adding sodium carbonate leads to strontium carbonate being precipitated from the solution.

The double decomposition process was established by Urguhart in 1884 (Ober, 1995). The reaction takes place between the fine celestite powder and sodium or ammonium carbonate solution at a temperature of about 90 °C. Because of the higher thermodynamic stability and lower solubility of strontium carbonate compared with strontium sulfate, during the reaction, the latter transforms to the former, as shown by the equation below,



The formed SrCO₃ is a mixed intergrowth with gangue minerals, but can be easily separated from the solid residue by dissolution with hydrochloric acid. After further purification of the strontium chloride solution, strontium carbonate is precipitated through the addition of sodium or ammonium carbonate. The schematic flow sheet is shown in Fig. 1.

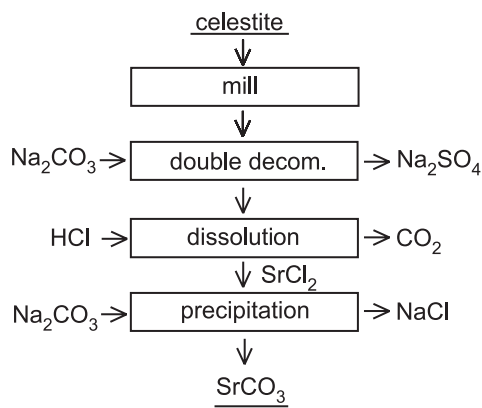
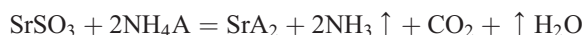


Fig. 1. Schematic flow sheet of double decomposition process for production of strontium carbonate from celestite.

Higher consumption of hydrochloric acid and sodium carbonate makes the process uneconomic. An improvement has been invented by taking a well-known decomposition method of strontium carbonate used in analytical chemistry. In this method, strontium carbonate reacts with a solution containing a high concentration of an ammonium salt with anions that could form soluble salts with strontium ions. The formed ammonium carbonate is driven away as NH₃ and CO₂ simultaneously, with only the soluble strontium compound left in solution (Xiong and Ling, 1988). The overall reaction is expressed as:



where A is an anion such as NO₃⁻, Cl⁻, S²⁻, HCOO⁻ and CH₃COO⁻.

NH₃ and CO₂ are then absorbed in water to form ammonium carbonate, which is recycled for double decomposition of celestite. Although this improved process has the advantage of eliminating acid use and reducing the consumption of carbonate, the evaporation to release ammonium carbonate is energy-intensive. Later, the inventors (Xiong and Ling, 1991) proposed to heat the crude strontium carbonate and an ammonium salt, such as ammonium chloride, at 700 °C to form strontium chloride and sublime ammonium carbonate. Some other researchers suggested decomposing the produced crude strontium carbonate at a higher temperature of 900–950 °C, forming SrO and CO₂. SrO was then hydrolyzed to form Sr(OH)₂ and then to precipitate SrCO₃ with CO₂ obtained from the decomposition (Chen and Li, 1988). However, the energy cost for decomposition is extremely high. Double decomposition of celestite with carbonate in a continual counter-current reactor has been patented (Proinsur, 1992). Purification of strontium solution with solvent extraction has been carried out in this laboratory (Xu and Zhu, 2002).

Obviously, the key to making the double decomposition process economically viable is to further reduce energy consumption during the recycling of acid and carbonate. Accordingly, we proposed to precipitate strontium carbonate from a neutral solution—for instance, strontium chloride or nitrate—with carbon dioxide and remove the produced acid by solvent extraction at the same time (Zhu and Xin, 2000). The stripped acid would then be recycled to

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