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Technology Summary: Vanadium Extraction from Black Shale

Opportunity Statement

Vanadium is a strategic material, used predominantly for high-strength steel alloys, as it imparts strength, hardness and corrosion resistance to the steel. Another important use of vanadium lies in making non-ferrous alloys, principally titanium. The titanium-vanadium alloys are used in jet engines, airframes, rockets, golf clubs and nuclear applications. A third use of vanadium lies in the chemical industry, especially in the production of sulfuric acid by the contact process. Vanadium can also be used in plastics, dyes, pigments, dietary and glass. An emerging application for vanadium is the energy storage market as a cathode material for vanadium batteries.

The primary sources of vanadium are vanadium titanomagnetite and black shale. Black shale is carbonaceous shale containing various materials such as vanadium, nickel, molybdenum and silver. The common grade of vanadium in this ore is usually less than 2%. Black shale is also commonly referred to as "stone coal" in China as it is mined as an energy source.

Problem

There have been several methods of vanadium extraction from black shale, including chloridizing, roasting, water leaching, deposition, alkali melting and thermal decomposition. These technologies suffer from one or both of two problems: low recovery of vanadium and serious environmental pollution. Treating shale with these methods often involves large volumes of chlorine (Cl) or hydrochloric acid (HCl), which are harmful for the environment.

Therefore, there is a need for the development of a process that can be used to efficiently extract vanadium and silicate from black shale in a cost-effective, environmentally safe manner.

360ip Partner's Solution

360ip's partner for this opportunity is Central South University (CSU), the #1-ranked applied research university in China. CSU's technology provides a method to extract vanadium pentoxide (V_2O_5) and calcium silicate (Ca_2SiO_4) from black shale. CSU's method involves the following steps:

1. Milling: Black shale is ball milled into a fine powder.

2. Oxidizing and roasting: The grinded powder is passed through a mesh and is oxidized as well as roasted in a muffle furnace. In the muffle furnace, material is isolated from the fuel and all products of combustion, including gases and flying ash.

3. Decomposing in sub-molten solution: The oxidized and roasted black shale is decomposed in a sub-molten salt solution of sodium hydroxide (NaOH) + sodium nitrate ($NaNO_3$). The sub-molten solution has good liquidity and high reactivity. It is easier to separate sodium vanadate ($NaVO_3$) from NaOH solution as the solubility of $NaVO_3$ in NaOH decreases with the increasing concentration of NaOH.

4. Dilute: The decomposed material is then diluted in water (H_2O) or diluted in NaOH solution. A solid phase constituting sodium silicate (Na_2SiO_3) and $NaVO_3$ is obtained and the remaining NaOH solution is recycled back to the sub-molten decomposing process.

5. Leaching: The solid phase obtained after dilution is heated in H_2O with NaOH as the leaching solution. Na_2SiO_3 and $NaVO_3$ dissolve in the solution and are separated from other sediments (Fe, Mg, Ca) and sodium aluminosilicate ($AlNa_{12}SiO_5$). The byproducts are sent for smelting. The pH value of the leaching solution containing Na_2SiO_3 and $NaVO_3$ is regulated to a value of 8–9. Ammonium chloride (NH_4Cl) is added into the leaching solution to obtain ammonium metavanadate (NH_4VO_3) sediment and Na_2SiO_3 solution.

6. Preparation of V_2O_5: NH_4VO_3 sediments are separated from the sodium silicate solution and burned under a high temperature. V_2O_5 is extracted which can be used in preparing vanadium products.

7. The making of calcium silicate: The Na_2SiO_3 solution obtained after leaching is treated with calcium hydroxide ($Ca(OH)_2$). This results in the formation of NaOH solution and Ca_2SiO_4. NaOH is recycled back to the decomposing process and Ca_2SiO_4 is used as a raw material for white carbon black. Thus, there is no NaOH loss as it is recycled back, which in turn reduces raw material consumption.

The complete process flowchart is provided on the following page.

Compared to existing methods, CSU's technology has the following advantages:

- Simple process that requires less time (3-8.6 hours, excluding grinding time as grinding is present in all other processes and consumes almost the same amount of time in each process).
- Low raw material consumption because of the recycling of NaOH and alkali solution. This results in lower production cost.
- Superior environmental benefits as NaOH and $NaNO_3$ are used instead of Cl and HCl in the initial stage.
- Results in a second valuable end product (Ca_2SiO_4).
- Competitive recovery and purity rates.

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Patents

360ip’s partner has filed one patent application on this technology and plans to seek protection in multiple jurisdictions.

360ip is seeking interested parties for the licensing, further development and commercialization of this technology-based product.

For additional information, contact:

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