SUBTASK 1.23 – MERCURY REMOVAL FROM BARITE FOR THE OIL INDUSTRY

Final Report

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DISCLAIMER

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ABSTRACT

Drilling muds are used by the oil and gas industry to provide a seal and to float rock chips to the surface during the drilling process. Barite (naturally occurring barium sulfate ore) is commonly used as a weighting agent additive in drilling muds because it is chemically nonreactive and has a high specific gravity (between 4.2 and 4.25 at 20°C). Because of environmental concerns, barite used by the oil and gas industry in the Gulf of Mexico must be certified to contain less than 1 mg/kg of mercury. Faced with these regulations, the U.S. Gulf Coast oil industry has looked to foreign sources of low-mercury barite, primarily India and China. These sources tend to have high-grade barite deposits and relatively inexpensive domestic transportation costs; as of late, however, U.S. purchasers have been forced to pay increasing costs for shipping to U.S. grinding plants. The objective of this project was to demonstrate two mercury removal techniques for high-mercury barite sources. Two barite samples of unique origins underwent processing to reduce mercury to required levels. The chemical treatment with dilute acid removed a portion of the mercury in both barite samples. The desired concentration of 1 mg/kg was achieved in both barite samples. An economic analysis indicates that thermal removal of mercury would not significantly add to the cost of barite processing, making higher-mercury barite a viable alternative to more expensive barite sources that contain lower concentrations of mercury.

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EXECUTIVE SUMMARY

Drilling muds are used by the oil and gas industry to provide a seal and to float rock chips to the surface during the drilling process. Barite (naturally occurring barium sulfate ore) is commonly used as a weighting agent additive in drilling muds because it is chemically nonreactive and has a high specific gravity (between 4.2 and 4.25 at 20°C). Because of environmental concerns, barite used for drilling in the Gulf of Mexico may be discharged into the water only if it is certified to contain less than 1 mg/kg of mercury. The mercury concentration of barite can depend on the region of the source in addition to other factors. Some barites have been confirmed to contain mercury concentrations above 10 mg/kg. Faced with these regulations, the U.S. Gulf Coast oil industry has looked overseas for low-mercury barite, primarily to India and China. These sources tend to have high-grade barite deposits and relatively inexpensive domestic transportation costs; as of late, however, U.S. purchasers have been forced to pay increasing costs for shipping to U.S. grinding plants.[1]

The primary goal for this project was to demonstrate at least two techniques for the economical removal of mercury from barite. To achieve this goal, two foreign barite samples known to contain over 1 mg/kg mercury underwent processing to remove mercury. Baseline mercury measurements and subsequent mercury analyses were conducted using an ASTM International acid extraction/cold-vapor atomic absorption method. Treated and untreated barite samples were subjected to other analyses to determine to what extent mercury removal techniques affected the structure of the barites.

An economic analysis was performed to determine whether treatments to remove mercury from heavy-metal barite sources were a viable option when compared to shipping low-mercury barite to U.S. grinding plants before use in the Gulf of Mexico. The price of importing barite from foreign sources for the Gulf of Mexico ranged from about $64/ton for Chinese barite to about $70/ton for Indian barite in 2004. Domestic sources of barite were valued at about $35/ton.[2] Most domestic barite, however, is currently not used in the Gulf of Mexico. Actual mercury reduction costs will depend on the type of barite and the amount of mercury it contains and the efficiency of the removal method.

[1] U.S. Geological Survey. *Mineral Commodity Summaries 2007: U.S. Geological Survey*; http://minerals.usgs.gov/minerals/pubs/mcs/2007/mcs2007.pdf (accessed Apr 2007), 195 p.

[2] Miller, M.M. Barite. U.S. Geological Survey Minerals Yearbook—2005. http://minerals.usgs.gov/minerals/pubs/commodity/barite/baritmyb05.pdf (accessed Apr 2007).

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INTRODUCTION AND BACKGROUND

When the oil industry drills for oil, a rotating drill bit is commonly used to penetrate the earth's crust. The oil industry uses drilling fluids, or muds, to lubricate and cool the drill bit, move the drill cuttings to the surface, provide a seal, and control downhole pressure (1). Most offshore oil wells are drilled using water-based drilling fluids, which are aqueous slurries of barite, clay, formation solids, and other materials (2). Used as a weighting agent, barite is a preferred component in drilling muds because of its high specific gravity (between 4.2 and 4.25 at 20°C) and chemical nonreactivity.

Barite, or barium sulfate, occurs naturally and is mined throughout the world. Most barite contains some mercury, with concentrations varying from as much as 10 mg/kg to less than 1 mg/kg, based on its location of origin (3). According to the offshore effluent limitation guidelines set forth by the U.S. Minerals Management Service and Environmental Protection Agency, "facilities located more than 3 miles from shore…may discharge drilling fluids and drill cuttings…(if) the barite component used to make the drilling fluid (does) not contain more than 1 mg/kg mercury…" (4). Faced with these regulations, the U.S. Gulf Coast oil industry has looked to foreign sources for low-mercury barite. These sources tend to have high-grade barite deposits and relatively inexpensive domestic transportation costs; as of late, however, U.S. purchasers have been forced to pay increasing costs for shipping to U.S. grinding plants (5).

For analytical purposes, Trefry et al. (6, 7) demonstrated that the mercury in various samples of barite were very stable in the marine environment but could be removed by rigorous acid leaching techniques. Previous work at the Energy & Environmental Research Center (EERC) (3) studied the mineral associations of mercury in different barites and verified that acid treatments were needed to remove the mercury in the barites. The regulatory requirements in the Gulf of Mexico and any future regulatory requirements will potentially limit the use of barite from many sources and drive prices up even further. A cost-effective way to reduce the mercury concentration in domestic barite to 1 mg/kg could supply the barite market with a cost-effective alternative to high-priced foreign barite.

PROJECT GOAL

The primary goal for this project was to demonstrate techniques for the economical removal of mercury from barite. The results from parametric evaluations are to be used as inputs for making cost comparisons of the mercury removal techniques. These results are to be compared with purchasing and shipping low-mercury barite.

ENVIRONMENTAL IMPACTS

One concern in the mercury removal process is the fate of mercury once it is released from the barite. To lower the mercury concentration of 1 ton of Scottish barite to a concentration of 1 mg/kg, 6.18 g of mercury would be released. To do the same with Spanish-origin barite would release 2.37 g of mercury. Grinding plants on the Gulf Coast of the United States typically grind imported barite for use in Gulf of Mexico applications. In 2005, the 14 plants on the coast that produced barite to American Petroleum Institute (API) specifications processed a total of 2.69 million metric tons or an average of 192,000 metric tons per plant (8). At that rate of processing, if one or more coastal grinding plants were to switch to a higher-mercury domestic barite (containing between 3.37 and 7.22 mg/kg mercury), each plant would release 455–1200 kg of mercury annually. The Clean Air Act requires that major pollution sources emitting 10 tons a year or more of a single air toxic "reduce emissions of toxic air pollutants from industrial, commercial, and institutional boilers and process heaters" (9). Treatment of barite would release mercury emissions much lower than the 10 tons a year threshold. Therefore, mercury emissions at barite grinding plants would not be required to be regulated, although voluntary emissions reductions would be recommended. Using a sorbent bed (e.g., activated carbon) would be a low-cost and effective strategy.

CONCLUSIONS

- The baseline mercury concentration of the Scottish sample was analyzed at 7.18 mg/kg, and the Spanish barite at 3.37 mg/kg.
- The target 1 mg/kg mercury was reached for the both barite samples after they underwent the mercury removal treatment.
- The treatment employed would still allow the barites to be used in drilling muds, since the resulting specific gravities were above the API standard of 4.2.
- Mercury emissions at barite grinding plants would not be high enough to require regulation. A sorbent bed such as activated carbon would be a low-cost and effective way to voluntarily reduce emissions.
- In terms of energy costs, treatment for mercury reduction would add less than $5/metric ton to the cost of the Scottish barite and less than $3/metric ton to the cost of the Spanish barite. These sources, however, would not be sustainable for a long period of time, making them unattractive to drilling companies.

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