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3,481,695 PROCESS FOR EXTRACTING ALUMINUM VALUES FROM OIL SHALE

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4 Claims

ABSTRACT OF THE DISCLOSURE

Oil shale is mixed with sodium chloride, sodium carbonate or bicarbonate salts or minerals, and the mixture is retorted to drive off the oil. The residue is leached with water or dilute mineral acid or base to extract aluminum values therefrom.

It has been recently discovered that the large deposits of oil shale in this country, particularly those in Colorado, contain, besides oil shale, substantial amounts of aluminum mainly in the form of dawsonite $[\text{NaAl}(\text{OH})_2\text{CO}_3]$. The aluminum also occurs in the shale in the form of feldspar, clay, and analcime. Further, it is believed that some aluminum occurs in amorphous forms, such as aluminum hydroxide, and as organo-metal complexes in the organic matter of the oil shale.

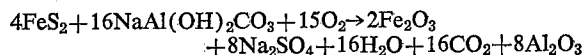
While investigating the economic potential of the oil shale as an aluminum source, it was discovered (see copending U.S. application Ser. No. 749,968 filed Aug. 5, 1968) that retorting the oil shale to at least about 400° C. to drive off the organic matter also converted large amounts of the dawsonite to water-soluble sodium aluminate. Likewise, it was discovered that dilute acid or base extracted large amounts of aluminum from the ash or residue. However, while practicing the process described in said application, it was observed that there was considerable variation, from one shale sample to another, in the percentage of each sample's total aluminum content which could be removed by leaching. In many instances the amount of aluminum recovered did not even equal the amount of aluminum present in the shale as dawsonite (the principal aluminum contributor).

I have now discovered that the aluminum recovery in the process described in copending patent application Ser. No. 749,968 can be improved at least to the point where the recovered aluminum is equal to the amount of aluminum present in the oil shale as dawsonite. Basically my process comprises adding, to the dawsonite raw shale, prior to retorting, sodium ion in the form of, for example, sulfur-free sodium salt such as sodium carbonate or sodium chloride, and then retorting at about 300° C–700° C., preferably at least about 400° C. After the organic matter is driven off, aluminum is readily extracted with water or dilute acid or base. Further, I have discovered that the addition of a sulfur-free sodium salt such as sodium carbonate to aluminum-containing, non-dawsonitic oil shale will substantially increase the yield of water-extractable or dilute alkaline solution-extractable or dilute mineral acid-extractable aluminum.

My process is based on the following observations and determinations:

In most of the oil shales tested under the process described in said copending application, it was found that the amount of sodium in the water leachate was approximately equal to the amount of sodium in the dawsonite in the raw shale. Further, when the leachates were evaporated to dryness, the sodium was found as sodium sulfate. Since sulfate minerals have not been discovered in raw shale, it was assumed that the main source of sulfur is

pyrite (FeS_2), which is ubiquitous in the shale in amounts ranging from 1 to 10%, or possibly organic sulfur compounds or other sulfide minerals. Thus, it was concluded that some of the dawsonite in the process described in said copending application reacts, during retorting, in the following manner:



Accordingly, it seemed that in any shale sample, the percentage of dawsonite that reacts with pyrite to form sodium sulfate rather than decomposing to water-soluble sodium aluminate depends on the amount of pyrite in the sample. This conclusion was further evidenced by the fact that in the practice of the process described in the above-mentioned copending application, the amount of extractable aluminum decreased as the sulfur content of the dawsonitic oil shale increased. Operating on these theories, I added other compounds of sodium to the oil shale in sufficient amounts (with regard to sodium ion) to satisfy the needs of the sulfate ion released by decomposition of pyrite during retorting. This resulted in a marked increase in the water-soluble aluminum.

In the case of aluminum-bearing, non-dawsonitic oil shale, it is believed that the addition of sodium carbonate-type compounds or sodium chloride to the raw shale retards, during retorting, the formation of difficult-to-extract alumina from amorphous aluminum hydroxide, thereby allowing greater extraction of the hydroxide form of aluminum by water or dilute acid or base leaches. Further, it is believed that the addition of sodium compounds might prevent, during retorting, the loss of organo-aluminum complexes which otherwise volatilize.

It is therefore an object of this invention to increase the amount of water-soluble sodium aluminate formed during retorting of dawsonitic oil shale. Another object is to prevent pyrite or organic sulfur substances from reacting with dawsonite during retorting of dawsonitic oil shale. A further object is to increase the amount of water-soluble or dilute acid-soluble or dilute alkaline solution-soluble aluminum values formed during retorting of aluminum-containing, non-dawsonitic oil shale. Other objects and advantages will be obvious from the following more detailed description of the invention.

In the practice of the invention with regard to dawsonitic oil shales, the amount of sulfur in the shale is first determined by standard chemical analysis techniques. From this determination, it can be calculated how much sodium will theoretically be required to convert all the sulfur to sodium sulfate. Next it is determined by analysis how much (if any) sodium in sodium-containing minerals other than dawsonite are present in the shale. In this respect, much of the rich Colorado oil shale contains nahcolite (NaHCO_3). If the sodium from non-dawsonitic sources in the shale is not at least equal to the previously calculated amount of sodium required to convert all the sulfur to sodium sulfate, then more sodium ion is added to the shale prior to retorting to make up for this deficiency. Exemplary sources of the sodium are sodium bicarbonate, sodium chloride, sodium carbonate, nahcolite (NaHCO_3), trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), shortite [$\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$], gaylussite



and halite (NaCl).

The following examples illustrates the effectiveness of the process of the present invention on dawsonitic oil shales:

EXAMPLE 1

Sample A of Piceance Creek Basin (Colorado) dawsonitic oil shale having about 1.6 wt. percent sulfur and being free of nahcolite was fired with and without the addition of sodium compounds at 600° C., and held at this temperature for 2 hours. After cooling to room temperature, each residue was leached 15 minutes with boiling distilled water (50 mls. water per gm. of residue). The residue from each water leach was then boiled 30 minutes in 150 mls. of 2% NaOH.

Sample B of Piceance Creek Basin dawsonitic oil shale having 1.0 wt. percent sulfur and being free of nahcolite was treated in the exact same manner as sample A.

All leaches from samples A and B were analyzed for aluminum by atomic absorption and the following results were obtained:

TABLE 1

	Aluminum in water leachate, p.p.m.	Aluminum in NaOH leachate, p.p.m.	Total aluminum in both leachates, p.p.m.
Sample A per se.....	5,480	10,700	16,180
Sample A mixed with nahcolite (.10 part nahcolite/part Sample A).....	9,305	8,400	17,705
Sample A mixed with trona (.10 part trona/part Sample A).....	8,105	7,050	15,155
Sample B per se.....	330	15,800	16,130
Sample B mixed with nahcolite (.10 part nahcolite/part Sample B).....	4,145	14,500	18,645

As can be seen from these results there is a marked increase in water-soluble aluminum compounds produced by the addition of sodium compounds to the dawsonitic raw shale.

In the practice of the invention with aluminum-containing, non-dawsonitic oil shale, sodium carbonate compounds in the form of, for example, nahcolite, trona, halite, shortite or gaylussite are mixed with the shale prior to retorting preferably in amounts ranging from about .20 to about .05 part additive per part of shale. Thereafter, the shale is retorted. A retorting temperature of about 300° C. to 700° C. held for about .5 hour to about 8 hours is suitable. The residue (preferably hot) is leached with dilute alkaline solution such as NaOH or dilute acid such as H₂SO₄ or HCl. The leaching medium is generally employed in amounts ranging from about 10 to about 20 parts leaching medium per part residue.

The following example illustrates the effectiveness of the present invention on non-dawsonitic oil shale:

EXAMPLE 2

Sample C, a non-dawsonitic oil shale from Piceance Creek Basin was treated in the same manner, with and without the addition of sodium compounds, as Sample A and B. The leachates had the following analysis:

TABLE 2

	Aluminum in water leach, p.p.m.	Aluminum in NaOH leach, p.p.m.	Total aluminum in leach, p.p.m.
Sample C per se.....	20	350	370
Sample C mixed with nahcolite (.10 part nahcolite/part Sample C).....	575	580	1,155
Sample C mixed with trona (.10 part trona/part Sample C).....	940	700	1,640

The marked effect of the sodium additive on non-dawsonitic oil shale is readily evident from Table 2. The total aluminum recovery was more than doubled by the sodium mineral additives.

Whether or not the oil shale is dawsonitic or non-dawsonitic, once the aluminum-bearing leachate solution has

been formed, it is only necessary to employ known procedures, such as carbonation to precipitate aluminum hydroxide and calcination to produce alumina, to recover the aluminum in desired form.

The following example illustrates the beneficial effects of the present invention on the production of shale oil during retorting.

EXAMPLE 3

Dawsonitic oil shale from Piceance Creek Basin and non-dawsonitic oil shale from the Mahogany Ledge in the Anvil Points Mine near Rifle, Colo. were obtained. These shales were ground to minus 8 mesh, and then mixed (100 parts shale) with 10 parts of nahcolite or trona which was ground to minus 20 mesh. The mixtures were then tested by Fischer assay (U.S. Bureau of Mines Report of

Investigations No. 4477) and analyzed for sulfur. The following results were obtained:

TABLE 3

Mixture	Sulfur in shale oil, percent
Dawsonitic oil shale per se.....	1.04
Plus trona.....	0.61
Plus nahcolite.....	0.98
Anvil Points oil shale per se.....	.57
Plus trona.....	.18
Plus nahcolite.....	.50

As can be seen from Table 3, some sodium additives employed in the process of the present invention have a marked effect on the shale oil produced from retorting. Thus, besides the aluminum-recovery advantages, the process also offers the advantage that it will eliminate the formation of H₂S or SO₂ which will otherwise be produced from pyrite or other sulfur compounds during the oil-shale retorting operation. This helps to overcome a serious air pollution problem and simultaneously improves oil quality by reducing sulfur contamination of the shale oil.

While the process is well adapted to carry out the objects of the present invention, it is to be understood that various modifications and changes may be made all coming within the scope of the following claims.

What is claimed is:

1. A process for recovering aluminum values from sulfur compound-containing and aluminum-containing dawsonitic oil shale comprising:

(a) mixing with said oil shale a sodium salt selected from the group consisting of sodium carbonate, so-

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dium bicarbonate, sodium chloride and mixtures thereof; said salt being added in a quantity which, when included with non-dawsonitic sodium present in said shale, is sufficient to theoretically convert all of the sulfur in said shale to sodium sulfate;

- (b) retorting said mixture at a temperature of at least about 300° C. to form a residue; and
 - (c) leaching said residue with a leaching medium selected from the group consisting of water, dilute mineral acid and dilute alkaline solution to leach out said aluminum; and then
 - (d) separating leachate solution containing said aluminum from remaining residue.
2. The process of claim 1 wherein said retorting temperature is about 300° C. to about 700° C.
 3. The process of claim 2 wherein said retorting temperature is at least about 400° C.
 4. A process for recovering aluminum values from non-dawsonitic aluminum-containing oil shale comprising:
 - (a) mixing with said shale a sodium salt selected from the group consisting of sodium carbonate, sodium bi-

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carbonte, sodium chloride and mixtures thereof; said salt being added in an amount of about .05 to about .20 part sodium salt per part of oil shale;

- (b) retorting said mixture at a temperature of at least about 300° C. to form a residue;
- (c) leaching said residue with a leaching medium selected from the group consisting of water, dilute mineral acid, and dilute alkaline solution to leach out said aluminum; and then
- (d) separating leachate solution containing said aluminum from remaining residue.

References Cited

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HERBERT T. CARTER, Primary Examiner

U.S. Cl. X.R.

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