FLOTATION PROCESS FOR SEPARATING BITUMINOUS MATTER FROM ASSOCIATED GANQUE MINERALS

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OIL SHALE

WATER

CRUSHER

SODIUM SILICATE

COAL TAR CREOSOTE

BALL MILL

PULP

PERCHLORETHYLENE

CONDITIONER

NON-REACTIVE FROTHER (Long chain alcohol)

PINE DISTILLATE (Monocyclic terpene hydrocarbons)

FLotation MACHINE (Primary Flotation)

FROTH (Rougher Concentrate)

TAILS

DUTCH CONE

+200 MESH -200 MESH

FLOCCULANT

TO WASTE

TANNIN (if calcite present)

CONDITIONER

NON-REACTIVE FROTHER (Long chain alcohol)

PINE DISTILLATE (Monocyclic terpene hydrocarbons)

FLotation MACHINE (Secondary Flotation)

FROTH (Concentrate)

TAILS

TO WASTE

FLotation MACHINE (Concentrate Cleaning)

FROTH (Finel Concentrate)

TAILS

TO WASTE

END PRODUCT

(Kerogen, Asphalite Paraffine Concentrate)

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ROGER DERING.

ATTORNEYS
This invention relates to processes of flotation, and is particularly concerned with the separation by flotation of bituminous or organic carbonateous materials, such as kerogen, asphaltries, and paraffines, from the host rock or other earth materials with which they are associated in nature.

In my copending application Serial No. 485,215, now Patent No. 2,890,795, filed January 31, 1955, entitled, "Metallurgical Processing of Uranium Ores," I have disclosed certain aspects of the present invention as a part of the over-all processing of uranium ore for the recovery of uranium values. There, the organic carbonateous material, usually asphaltite, carries uranium values, but is separated from uranium-bearing inorganic portions of the ore by flotation so that it may be independently processed for the recovery of the uranium.

I have found that essentially the same flotation procedure is applicable to the recovery of organic carbonateous materials, such as kerogen and associated asphaltite and paraffine found in oil shales, the bituminous material in bituminous sands and sandstone, and the asphaltic material in asphaltic shales, when those are the values sought.

A principal object of this invention is to provide a flotation process for effectively separating, organic carbonateous materials from rock and other inorganic mineral matter with which they are intimately associated.

A more specific object is to provide a practical, commercial process for producing from oil shale a high-kerogen material for conversion into shale oil and other products.

An outstanding feature of the invention is the subjecting of a flotation pulp of the material to flotation in the presence of a suitable pine distillate and a super-normal quantity of a coal tar creosote. The carbonateous material is floated off as a froth concentrate.

Further objects and features will become apparent from the following detailed description of the presently preferred procedure illustrated by way of example in the accompanying drawing.

In the drawing, the single FIGURE is a flow sheet showing the preferred procedure as applied to oil shale.

The kerogen content of oil shale is in the form of solid particles distributed throughout the fine-grained, sedimentary, host rock. Oftentimes asphaltite and paraffine residues are physically associated with the kerogen. These organic carbonateous materials are not readily wettable, although the associated rock may be easily wetted in accordance with long established practice in the flotation art.

As indicated in the flow sheet, the shale is first crushed and ground to a size suitable for flotation, e.g. to minus 80 mesh. The secondary crushing stage is carried out wet to prevent pyrolysis. Grinding should not be excessive, and, to this end, is preferably carried out with large balls or rods.

In accordance with the invention, a super-normal quantity (e.g. 0.5–2.0 lbs./ton of ore depending upon the character of the ore) of coal tar creosote such as Barrett No. 4, is employed as a collector for the kerogen. Another special reagent having very little if any frothing properties is also employed as a promoter for the organic values. This is a complex combination of monocyclic terpene hydrocarbons normally derived from the destructive distillation of pine and containing pinenes and terpinenols. It has limited solvent properties with respect to the organic carbonateous matter to be recovered. An example of such material is the proprietary product "Solvone" marketed by Hercules Powder Co. It is used in quantity of from about 0.1 to 0.3 pound per ton of ore, depending upon the character of the ore, it being realized that the values sought are strongly hydrophobic and this reagent has a selective affinity therefor.

The material "Solvone" is somewhat variable in composition, but the following is typical:

<table>
<thead>
<tr>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinene and other bicyclic terpenes</td>
</tr>
<tr>
<td>Dipentene</td>
</tr>
<tr>
<td>para-Cymene</td>
</tr>
<tr>
<td>para-Menthanes and para-Menthanes</td>
</tr>
<tr>
<td>Terpinolene and other monocyclic terpenes</td>
</tr>
<tr>
<td>Low-boiling terpene alcohols and ketones</td>
</tr>
</tbody>
</table>

A silica depressant, such as sodium silicate, is also utilized where necessary, e.g. with oil and asphaltic shales and bituminous sands. It is not necessary with the uranium ores of my afore-referenced copending application. Both it and the coal tar creosote are preferably added to the pulp in the grinding circuit. From about 0.1 to 3.0 pounds per ton of ore are used depending upon the quantity and physical characteristics of the silica present.

The pulp from the grinding circuit is advantageously conditioned in the usual conditioning equipment with a tetrachloride, such as perchloroethylene, which acts as a depressant on barren colloidal slimes and also aids in loosening the wax and asphalt from association with the mineral particles. This reagent also exhibits some collection properties with respect to the kerogen and other organic carbonateous materials. From about 0.1 to 3.0 pounds per ton of ore are used depending upon the organic content and characteristics of the ore.

Following this conditioning stage, the pulp is subjected to primary flotation in the usual equipment, advantageously in the presence of a non-reactive, neutral frother selective as to the non-wetted bituminous particles. A long chain alcohol, such as Dowfroth 250 or Aerofroth 65 (both well known commercial reagents), is very satisfactory, although practically any of the well-known non-reactive frothers, such as pine oil, eucalyptus oil, and amyl acetate, may also be employed. From about 0.02 to 0.10 pound per ton of ore are used, depending upon the froth conditions and scavenging requirements. The special promoter reagent derivative mentioned above is preferably added here.

The froth contains the kerogen, asphaltries, and paraffines, and is recovered as a rougher concentrate which is sent to a cleaner cell to produce a final concentrate representing the final product of the operation. The tails from this primary flotation stage are desirably classified and scavenged in a Dutch cone, and the minus 200 mesh material passed to a second conditioning stage, where one of
the well-known flocculating agent, such as Dow "Separan 2610" or American Cyanamid "Aerofloc 548," is added as a slime depressant, and where, if calcite is present, a calcite depressant, such as a tannin derivative, is added in accordance with usual practice in the flotation art.

The so-conditioned tails are then subjected to secondary flotation, utilizing the "Solenvel" type of reagent in quantity of about 0.04 to 0.10 pound per ton of ore and the neutral selective frother (long chain alcohol) in quantity of about 0.10 to 0.15 pound per ton of ore. The concentrate from this secondary flotation is passed to the cleaner cell along with the rougher concentrate of the primary flotation, while the tails are passed to waste.

The cleaner flotation of concentrates is carried out using a slime depressant reagent (a poly-electrolytic settling agent, such as American Cyanamid "Aerofloc," or some other high molecular polymer flocculant such as Dow "Separan") and the aforementioned neutral selective frother in quantities of from about 0.01 to 0.05 and 0.01 to 0.10 pound per ton of ore, respectively.

The final concentrate is a high-kerogen material which may be processed in some suitable manner, as, for example, by retorting, to produce shale oil and other products.

The following example with respect to oil shale is typical of many laboratory tests carried out with substantially similar results:

**Example**

One kilogram of an oil shale taken from T-6-S, R-6-E near Soldier Summit, Utah, was crushed to 8 mesh and ground in a laboratory ball mill to minus 80 mesh. Coal tar creosote was added to the ball mill on the basis of 1/2 lb. per ton of ore. Sodium silicate (commercial) was added to the ball mill on the basis of 3 lbs./ton, along with one kilogram of water (100 gms. of water was added earlier in the secondary crushing stage using a gyrotary type, laboratory crusher). The ball mill discharge was conditioned six minutes with 1 lb./ton perchloroethylene (C₆Cl₄). The conditioned pulp was run into a 1000 gm. laboratory flotation cell, and 0.15 lb./ton of "Solenvel" added. The first stage of primary flotation was carried out for four minutes, after which 0.10 lb./ton of "Dowfroth 250" was added and a scavenging flotation stage carried out for four minutes.

The tails were scoured and classified. The plus 300 mesh material was discarded, but the minus 300 mesh material was conditioned for six minutes with 0.02 lbs./ton of "Separan 2610" and with 0.05 lbs./ton of Quebracho (a tannin derivative). The conditioned pulp was then passed to secondary flotation, where 0.05 lbs./ton of "Solenvel" and 0.05 lbs./ton of "Dowfroth 250" were added and flotation carried out for eight minutes. The tails were discarded.

The froth concentrates from both primary and secondary flotation were passed to cleaner flotation, and 0.05 lb./ton of "Aerofloc 548" and 0.05 lb./ton of "Dowfroth" were added. Flotation of these froth concentrates was carried out for twelve minutes.

The final froth was filtered and volatilized in an electric furnace, with the following results:

<table>
<thead>
<tr>
<th>Product</th>
<th>Percent Tannin</th>
<th>Percent Sodium Silicate</th>
<th>Percent Creosote</th>
<th>Perm Volatiles</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Shale</td>
<td>100.0</td>
<td>37.6</td>
<td>62.2</td>
<td>15.4</td>
<td>8.9</td>
</tr>
<tr>
<td>Filter Feed</td>
<td>41.2</td>
<td>68.8</td>
<td>31.2</td>
<td>15.4</td>
<td>8.9</td>
</tr>
<tr>
<td>Waste</td>
<td>56.5</td>
<td>8.8</td>
<td>94.2</td>
<td>8.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Ratio of concentration = 2.64:1.

It can be seen from these results that over 91% of the bituminous materials was recovered, while eliminating over 93% of the inorganic gangue. The percent volatiles was increased from over 37% in the raw shale to over 83% in the final material, indicating a ratio of concentration of 2.43:1.

When this process has been illustrated and described with respect to a particular preferred application thereof in practice, it should be realized that the invention is not limited to the specific procedures set forth, and that such procedures may be varied by those skilled in the art within the scope of the claims which here follow.

I claim:

1. A floation process for the separation of bituminous material, such as kerogen, asphalts, and paraffines, from associated inorganic gangue materials, comprising subjecting a flotation pulp of the materials to conditioning with a tetrachloride; subjecting the conditioned pulp to froth flotation in the presence of effective quantities of a complex of monomeric terpene hydrocarbons, derived from the destructive distillation of pine, and of coal tar creosote, to produce a froth which is high in bituminous materials and a tails which is low in bituminous materials; and separating said froth from said tails.

2. The flotation process of claim 1, wherein a silica depressant is also used as a reagent in the froth flotation of the bituminous materials.

3. The flotation process of claim 1, wherein a non-reactive, neutral frother (long chain alcohol) is also used in the froth flotation of the bituminous materials.

4. The flotation process of claim 3, wherein the tails are conditioned with a flocculating agent and subjected to secondary flotation with more of the special pine derivative reagent and long chain alcohol.

5. The flotation process of claim 4, wherein the froth from both the primary and the secondary flotation stages is subjected to cleaner flotation in the presence of a flocculating agent and more of the long chain alcohol.

6. A froth flotation process for the separation of the kerogen and other bituminous content of oil shale from the rock with which they are associated, comprising subjecting a flotation pulp of an oil shale to conditioning with a tetrachloride; subjecting the conditioned pulp to froth flotation in the presence of an effective quantity of a complex of monomeric non-reactive neutral frother reagent selective to the kerogen and other bituminous materials.

7. The flotation process of claim 6, wherein the non-reactive neutral frother reagent is a long chain alcohol.

8. A flotation process for the separation of bituminous material, such as kerogen, asphalts, and paraffines, from associated inorganic gangue in an ore material, comprising subjecting a flotation pulp of the ore material to froth flotation in the presence of a complex of monomeric non-reactive neutral frother hydrocarbons derived from the destructive distillation of pine, and effective quantities of coal tar creosote, of a silica depressant, and of a non-reactive neutral frother reagent selective to the kerogen and other bituminous materials.

9. A froth flotation process for the separation of the kerogen and other bituminous content of oil shale from the rock with which they are associated, comprising subjecting a flotation pulp of an oil shale to froth flotation in the presence of a complex of monomeric non-reactive neutral frother hydrocarbons derived from the destructive distillation of pine and in quantity of from about 0.1 to 0.3 pound per ton of ore material, coal tar creosote in quantity of from about 0.5 to 2.0 pounds per ton of ore material, and a non-reactive neutral frother in quantity of from about 0.2 to 1.0 pounds per ton of ore material, to produce a froth which is high in bituminous material and a tails which is low in bituminous material said complex having very little or no frothing characteristics as compared with pine oil and having only limited solvent action with respect to said bituminous material; and separating said froth from said tails.

10. A froth flotation process for the separation of the kerogen and other bituminous content of oil shale from the rock with which they are associated, comprising subjecting a flotation pulp of an oil shale to froth flotation in the presence of a complex of monomeric non-reactive neutral frother hydrocarbons derived from the destructive distillation of pine and in quantity of from about 0.1 to 0.3 pound per ton of oil shale, coal tar creosote in quantity of from about 0.5 to 2.0 pounds per ton of oil shale and a non-reactive neutral frother reagent selective to the kerogen.
and other bituminous materials, said frother reagent being used in quantity of from about 0.02 to 0.10 pound per ton of oil shale.

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