This invention relates to a method of recovering sulfur from native sulfur-bearing ores; that is, from ores which contain free elemental sulfur. The principal object of the invention is to provide a process which will extract substantially all of the sulfur from the ore, with recoveries from a single cycle on the order of 90% or better, and which will produce a commercially pure sulfur.

There are many deposits of native sulfur-bearing ores throughout the world which are sufficiently rich in sulfur to warrant commercial development if a satisfactory recovery and purification process were available. Typical of these are deposits in Colombia, in Egypt, and in the island of Milos, all of which have a free sulfur content within the range of about 20-35% or better. Attempts have previously been made to separate this sulfur from ores of this type by melting and agglomeration processes, in which the ore is heated to a temperature above the melting point of sulfur (113-120°C.) to cause the sulfur droplets to run together and separate from the ore. However, these processes are not commercially usable with some ores, notably those containing the sulfur in a finely divided form throughout the ore, as in Egyptian ores. Moreover, the sulfur recoveries obtainable by these processes seldom exceed 50-75%, and even with the most favorable ores, a recovery of about 80% of the sulfur is the best that can be obtained.

One of the principal reasons for the relatively low recovery of sulfur by a simple melting and agglomeration process is the fact that a certain proportion of the molten sulfur is inevitably held in the interstices of the gangue. The present invention, while taking advantage of the principle of agglomeration separation to the extent that it can be used with the particular ore under treatment, provides an improved method of separating the sulfur phase from the gangue material. This is done by the use of froth flotation.

It has many times been proposed to separate sulfur from sulfur-bearing ore by grinding the ore and subjecting it to a froth flotation process. Attempts to carry out these proposals on a commercial scale, however, have always encountered difficulties caused by the presence of finely divided sulfur in the ground ore. During the grinding step a substantial proportion of the free sulfur in the ore is always disintegrated into fine sulfur particles which, during the flotation process, attach themselves to the bubbles of froth. By coating the surfaces of the bubbles, these fines stabilize the froth and reduce its ability to receive particles of gangue, thus impairing the selectivity of the flotation and lowering the grade of the concentrate produced.

The present invention overcomes all of the above difficulties and produces a pure sulfur with a high percentage of recovery by first heating and agitating an aqueous slurry of the ground sulfur-bearing ore for a short time at a temperature above the melting point of sulfur to cause the fine sulfur particles to coalesce into larger aggregates containing less exposed surface. The slurry is then cooled to a temperature below the melting point of sulfur and subjected to froth flotation, preferably at relatively high temperatures of about 50-100°C, followed by remelting and filtering the sulfur obtained in the flotation concentrate.

If the ore being treated is one from which a substantial proportion of the sulfur separates during the heating and agitating step, the sulfur so obtained may be drawn off as liquid sulfur during the heating step, or the agglomerated sulfur may be screened from a slurry after it has been cooled, either prior to or after flotation. In either event, the sulfur so obtained is preferably melted and filtered along with the sulfur from the flotation concentrate. We have found, however, as an important feature of the present invention, that the time of heating necessary to agglomerate the fine sulfur particles is much less than that which would be required to separate substantial quantities of liquid sulfur from the ore, and therefore only a very minor proportion of the sulfur is separated out in this manner during the practice of the preferred embodiments of our invention.

The invention will be further described with reference to the accompanying drawings, in which the single figure is a flow diagram in which the various steps of a complete process are illustrated.

In carrying out the process of our invention, a native sulfur-bearing ore such as any of those referred to above may be crushed and, if desired, may be given a preliminary beneficiation by any suitable process. It is then ground and screened with return of oversize to the grinding process, preferably to a maximum particle size within the range of 10-40 mesh, although finer grinding up to through 100 mesh or smaller may be used in some cases if this should prove to be desirable. It is, however, an important advantage of the invention that in most cases fine grinding need not be resorted to.

After the ore has been ground, which always causes some 50% or more of its sulfur content to
be disintegrated into fines having a particle size of on the order of 1–5 microns, the ground material is slurried in water. In most cases sufficient water is used to form a slurry of about 15–50% solids content; however, the concentration of the slurry is not critical and is usually kept as high as possible, consistent with the ability of a pump to force it into the coil or other heating vessel. When floation middlings from the process are recycled to the slurring step, their water content is of course considered in calculating the proper amount of water to be added to produce slurries of the desired density. Where hot water is available from the process, as is illustrated on the attached flow sheet, it may be used to form the slurry, thus reducing the amount of high-pressure steam consumed in the heating coil. Any suitable apparatus may be used for preparing the slurry, a tank 1 provided with an agitator 2 being diagrammatically illustrated on the drawing.

The slurry prepared in the tank 1 is forced through pipe 3 into a heating and agitating coil 4, preferably by means of a pump such as that shown at 51. Steam at 20–50 pounds per square inch gauge pressure, or higher, is introduced through pipe 6 and is mixed directly with the slurry in the pipe coil, while the turbulence created by its introduction and by passage of the mixture through the coil results in vigorous agitation. When the temperature of the slurry in the coil is above the melting point of sulfur, the sulfur fines produced in the grinding step are quickly agglomerated by adhesion to each other. We have found that under the conditions stated the agglomeration of the sulfur fines takes place very rapidly, a time of about 15–60 seconds usually being sufficient. The total time of sojourn of the slurry in the coil 4 is therefore usually within the range of from about 15 seconds to about 4–5 minutes, depending largely on the rate of heating, which in turn is dependent upon the initial temperature of the slurry and the pressure of the steam employed. It will be seen that this feature of our process can be carried out both continuously and at an extremely high production rate, as compared with prior sulfur recovery procedures where the heating was relied upon to separate the entire yield of sulfur from the ore. After the slurry has been heated for the required length of time in the coil 4 it should be cooled rapidly to a temperature below the melting point of sulfur, preferably below 100°C so that no boiling will occur when the pressure is released. This is preferably accomplished by injecting cold water into the slurry by means of the pipe 8 as it passed through line 30 and pressure-reducing valve 1. The conditioned slurry then discharges through pipe 8 into a storage tank 9. In this tank it may be diluted and adjusted to flotation density by the addition of water through the line 10. The normal pulp densities usually employed in froth flotation (i.e., about 20–25% solids) are utilized in practicing our invention.

The particles of agglomerated sulfur are separated from the gangue by a froth flotation process, with or without a preliminary screening. Conditioned slurry from the storage tank 9 is withdrawn through line 11 and may be screened, if desired, on a rotary screen 12 to remove oversized lumps of sulfur; this screen preferably has a mesh size of about the same as that used for screening the ground raw ore. Lumps of sulfur collected on the screen are introduced into the melter and sulfur filter that will be subsequently described, on a rotary screen 13, and may be eliminated from the process, the pulp from the storage tank 9 being passed directly to the flotation process.

Flotation of the conditioned ore pulp is preferably carried out in two or more flotation cells which are, for example, of the Fagergren type. These flotation machines consist essentially of a flotation chamber containing a stator composed of a ring of spaced vertical cylindrical bars, within which is mounted a cylindrical rotating cage having vertical sides that are also composed of spaced cylindrical bars. The top of the cage is attached to a hollow rotating shaft, through which air is drawn by the vortex action. The relative motion of the rotor bars past the stator bars effectively disseminates the occluded air into fine bubbles and evenly distributes them throughout the mass of the slurry. These fine bubbles collect the non-volatile sulfur particles in the pulp and raise them to the surface. Fine oil in amounts of 0.01–0.03 pound per ton of ore or sodium dicycldithiophosphate, or both, may be used as frothing or collecting agents in the flotation process. The flotation is carried out under acid conditions, the pH being maintained at about 3.0. As is noted above, greatly improved results are obtained when the flotation is carried out at 40–100°C, and, therefore, the pulp is passed through the flotation machines at a temperature within this range and preferably at 60–90°C. It is a peculiar advantage of the invention that the heat used to cause agglomeration of the fine sulfur particles in the cells 4 may also be used to improve the efficiency of the flotation.

The first flotation cell 14, or group of cells, is operated as a rougher, the tailings from this group being discarded. The concentrate is passed through a rougher or other conveying line 16 to one or more cleaner flotation cells 16 where it is again floated at about the same temperature to produce a semi-refined sulfur concentrate of about 80–95% purity, depending on the particular ore. The middlings, or tailings from the second flotation, are passed through line 17 to a thickener 18, from which the thickened pulp is returned through line 19 to mix with additional conditioned slurry in the pipe 20 for return to the rougher flotation 14. Alternatively the thickened middlings may be returned to the slurry tank 1. Overflow from the thickener 18 passes through lines 21 and 22 to the hot water storage tank 23. The tailings from the rougher flotation cells 14 are also thickened in a thickener 24, from which the overflow water passes through line 25 to the storage tank 23. The pulp withdrawn from the bottom of this thickener through line 26 is discarded.

The concentrate from the cleaned flotation cells 16 is passed through pipe 21 to thickener 22 from which the overflow water is also passed to the hot water storage tank 23 through line 27. The thickened pulp leaving through line 30 is dewatered on a filter 31 and is then heated, as by steam coils 32, in a melter 33, to which screenings from the screen 12 may also be added. The molten sulfur product leaving 33 is then passed through line 34 to a steam-heated sulfur filter 35, from which a filtrate consisting of commercially pure sulfur is recovered. For this purpose a leaf-type filter may be employed in which a plurality of filter leaves are immersed in the sulfur to be filtered, the purified sulfur being withdrawn from the interior of the leaves and the filter cake collecting on the outer surfaces thereof.
The foregoing is a description of the best method at present known to us for practicing the invention, but it should be understood that other types of equipment may be substituted for those illustrated diagrammatically in the drawing. Thus, for example, we have, obtained good results with some ores in a system in which the heating and agitating coil 4 is substituted by one or more pressure vessels equipped with internal agitators, wherein the ground ore slurry is heated by injection of steam at 20-50 lbs. gauge pressure and the agitation required to agglomerate the fine particles of molten sulfur is obtained by the mechanical agitators. A pressure vessel of this type is preferably equipped with a valve outlet at the bottom, so that liquid sulfur can be drawn off if it accumulates in the vessel. As a further alternative the slurry may be heated indirectly, as by a steam jacket surrounding the coil 4, instead of by the direct injection of steam. It will also be understood that the ore slurry, after being heated for about 0.25-5 minutes in the pipe coil, autoclave or other pressure vessel, can be cooled to a temperature below the melting point of sulfur by indirect cooling, as by passage through a pipe surrounded by a jacket of cooling water, if desired. Other forms of apparatus for carrying out the steps of the invention will readily suggest themselves to those skilled in the art.

Our experiments have shown, however, that for most native sulfur-bearing ores a pipe coil of the type illustrated in the drawings is greatly preferable, and therefore we will describe such a coil in detail. In obtaining the results shown in the following specific examples we employed a set of pipes of 3/4 inch internal diameter, covered with suitable insulation and joined at their ends by U-turns. At one end of the coil, valved pipes were inserted in the U-turns so that steam could be injected into each coil separately, while similar by-pass lines connected the U-turns at the opposite end of the coil to a common header. By opening and closing the valves in these by-pass lines the length of time of sojourn of the slurry in the heating coils could be adjusted. A total of seven 10-foot lengths of pipe were used in this coil arrangement with by-pass adjustments such that from a single length to the entire coil system could be adjusted as desired.

The invention will be further illustrated by the following specific examples of results that have been obtained with particular ores and under particular operating conditions. It should be understood, however, that although these examples may describe in detail some of the preferred embodiments of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

A sample of low grade ore from Colombia, S. A., containing about 33% of elemental sulfur in a volcanic silicate and oxide gangue was dry ground to pass through a 28 mesh screen. Approximately 2500 grams of this material were suspended in 7.5 liters of water to form a slurry of about 25% solids. This slurry was forced continuously through a coil of 1/4 inch pipe into which live steam at 30 lbs. per square inch gauge was injected, thereby heating the slurry to about 130° C. The residence time of the slurry in the coil was approximately 30 seconds, after which the slurry was immediately cooled to 85° C. by admixture with cold water.

A portion of the conditioned slurry containing 414 grams of solids was screened on a 28 mesh wire cloth, which retained 6 grams of sulfur having a purity of about 98%. The remaining slurry, containing 408 grams of solids, was subjected to flotation at 85° C. in a Fagergren batch flotation machine at a pulp density of about 20% solids using pine oil and sodium dicylithiophosphate. The flotation time required was less than 1 1/2 minutes.

The products obtained were:
(a) 158 grams dry weight of concentrate containing 122.4 grams of sulfur.
(b) 250 grams dry weight of tailings containing 7.2 grams of sulfur.

The tailings, representing a loss of 5.2% of the sulfur in the ore, were discarded. The concentrate was repurled with water at 65° C. to about the same flotation density and again separated from froth flotation into:
(c) 109 grams of concentrate (dry weight) containing 105 grams of sulfur.
(d) 49 grams of middlings (dry weight) containing 17.4 grams of sulfur.
(e) The middlings were refloated in admixture with a second portion of the conditioned and screened ore whereby 16.5 grams of its sulfur content were recovered in a product weighing 17.1 grams.

The final products were therefore:

<table>
<thead>
<tr>
<th>Grams</th>
<th>Grams</th>
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<tbody>
<tr>
<td>Screenings</td>
<td>6 Sulfur</td>
</tr>
<tr>
<td>(c)</td>
<td>109 Sulfur</td>
</tr>
<tr>
<td>(e)</td>
<td>17 Sulfur</td>
</tr>
<tr>
<td>Total</td>
<td>132</td>
</tr>
</tbody>
</table>

These products were melted together and pressure filtered through a glass filter cloth. The filtrate was 124 grams of sulfur having a purity of 99.5%. The filter cake contained approximately 50% of sulfur, most of which could be recovered by mixing it with raw ground ore in the original slurry tank.

The net result of this treatment was, therefore, that about 92% of the sulfur in the ore sample was recovered as a commercial product of 99.5% purity; about 3% of the sulfur was recirculated through the process, and about 5% was lost in the gangue.

Example 2

The procedure of Example 1 was repeated with the addition of varying quantities of ground raw ore to the flotation feed in order to demonstrate the adverse effect of the sulfur slimes so introduced.

To another portion of the conditioned (steam-treated) slurry of Example 1 there was added 100 grams of the raw ore at it existed just prior to the first step; i.e., after grinding and screening through a 28 mesh screen. The resulting pulp, without screening, was diluted with hot water to 20% solids and subjected to rougher and cleaner flotions at 85° C. and 65° C., with return of the middlings to the rougher flotation and filtration of the concentrates, exactly as described in Example 1. By this procedure there was obtained:
(a) 144 grams of commercial sulfur of 99.5% purity, equal to 82.8% of the sulfur in the ore.
7 (b) 325 grams of tallings, containing 6.3% of the sulfur in the ore, which were discarded.
(c) 38 grams of filter cake, containing 10.9% of the sulfur in the ore.

A third test was made in which only raw ore was used. 327 grams of unconditioned ore, ground and screened through the 28 mesh screen, was suspended in hot water to 20% solids and subjected to the treatments described above with the following results:
(d) 42 grams of 99.5% pure sulfur, equal to 36.6% of the sulfur in the ore, were recovered as filtrate.
(e) 153 grams of tallings containing 6.8% of the sulfur in the ore were discarded.
(f) 132 grams of filter cake, containing 57.6% of the sulfur in the ore.

Example 3

Another sample of the Colombian ore of Example 1 was ground and screened through a 28 mesh screen, slurried in water and treated with steam in the coal as described in that example, but the residence time in the cell was increased to 3 minutes. The only noticeable difference resulting from the longer heat treatment was that a larger proportion of the sulfur separated out during the screening prior to flotation.

The conditioned pulp was separated into several portions which were subjected to the flotation treatments described in Example 1 at different temperatures; the same pulp density being used throughout.

No. 1.—The ore was floated at 85° C. and the screenings and flotation concentrates were melded and filtered. The recoveries were:
(a) Approximately 156 grams of commercial sulfur, equal to 92.2% of the sulfur in the ore, were obtained as filtrate.
(b) 277 grams of tallings containing 4.7% of the sulfur in the ore were discarded.
(c) 11 grams of filter cake containing 3.1% of the sulfur in the ore were required recycling.

No. 2.—Flotation at 60° C. The results were:
(a) 137 grams of filtrate, equal to 88.5% of the sulfur in the ore.
(b) 369 grams of tallings containing 8.7% of the sulfur in the ore.
(c) 6 grams of filter cake containing 2.8% of the sulfur in the ore.

No. 3.—Flotation at 40° C. The results were:
(a) 145 grams of filtrate, equal to 88% of the sulfur in the ore.
(b) 290 grams of tallings containing 6.6% of the sulfur in the ore.
(c) 18 grams of filter cake containing 5.4% of the sulfur in the ore.

No. 4.—Flotation at 25° C. The results were:
(a) 128 grams of filtrate, equal to 74% of the sulfur in the ore.
(b) 298 grams of tallings containing 15.3% of the sulfur in the ore.
(c) 38 grams of filter cake containing 10.7% of the sulfur in the ore.

These tests show the importance of conducting the flotation at temperatures of at least 40° C., and preferably at 60–90° C. When the temperature is below about 40° C. the percentage of sulfur lost in the tallings increases rapidly and the grade of the flotation concentrate is low.

Example 4

A sample of a native sulfur-containing ore from the island of Milos, Greece, was treated by the procedure described in Example 1. In this ore the gangue was a rather pure siliceous volcanic ash. The products obtained were as follows:
(a) The filtrate was 67 grams of commercially pure sulfur; equal to 97.5% of the sulfur in the ore sample.
(b) 213 grams of tallings were discarded containing 0.9% of the sulfur in the ore.
(c) 2 grams of filter cake, containing 1.6% of the sulfur in the ore, required recycling.

Example 5

A sample of sulfur ore from the Gemsa peninsula of Egypt was treated by the process of Example 1. In this ore the sulfur was disseminated in the form of very fine particles throughout a gangue consisting of a mixture of silica and impure gypsum. The following products were obtained:
(a) 148 grams of sulfur of commercial purity, equal to 89.4% of the sulfur in the ore.
(b) 272 grams of tallings containing 6.9% of the sulfur in the ore.
(c) 12 grams of filter cake containing 3.7% of the sulfur in the ore.

What we claim is:
1. A method for recovering sulfur from a native sulfur-bearing ore which consists of the steps of grinding said ore, during which a portion of its free sulfur is disintegrated into fines, suspending the ground ore in water, heating the resulting slurry with agitation to a temperature above the melting point of sulfur for a period of from 0.25 to 5 minutes to cause said fines to coalesce, cooling the slurry to a temperature below the melting point of sulfur and subjecting it to a froth flotation at normal flotation pulp density, removing as flotation concentrate a semi-purified sulfur, and melting and filtering said semi-purified sulfur to produce a sulfur of 99–100% purity.
2. A method according to claim 1 in which the ore is ground and screened to a maximum particle size of 10–40 mesh and suspended in water to a slurry of about 20–50% solids.
3. A method according to claim 1 in which the slurry is heated by direct injection of steam to 120–135° C.
4. A method according to claim 1 in which the slurry, after cooling but before flotation, is screened to remove lumps of agglomerated sulfur and the lumps so removed are melded and filtered along with the semi-purified sulfur from the flotation concentrate.
5. A method according to claim 1 in which the flotation is carried out at a temperature within the range of 40–100° C.
6. A method of recovering sulfur from a native sulfur-bearing ore which consists of the steps of grinding and screening said ore to a maximum particle size of 10–40 mesh, during which a portion of its free sulfur is disintegrated into fines, suspending the ground ore in water, heating the resulting slurry with agitation to a temperature of 120°–135° C. and during a time of about 0.25–5 minutes to cause said fines to coalesce, cooling the slurry to a temperature below the melting point of sulfur and subjecting it to a froth flotation at
normal flotation pulp density, removing as flotation concentrate a semi-purified sulfur, and melting and filtering said semi-purified sulfur to produce a sulfur of 99-100% purity.

7. A method according to claim 6 in which the slurry, after cooling but before flotation, is screened to remove lumps of agglomerated sulfur and the lumps so removed are melted and filtered along with the semi-purified sulfur from the flotation concentrate.

8. A method according to claim 6 in which the flotation is carried out at a temperature within the range of about 60°-90° C.

9. A method of recovering sulfur from a native sulfur-bearing ore which consists of the steps of grinding said ore, during which a portion of its free sulfur is disintegrated into fines, suspending the ground ore in water, heating and agitating the resulting slurry to a temperature above the melting point of sulfur by forcing it during about 0.25-5 minutes through a narrow passage while injecting steam therein and thereby causing said fines to coalesce, injecting cold water into said slurry and thereby cooling it below the melting point of sulfur, diluting the slurry to normal flotation pulp density and subjecting it to froth flotation and removing as flotation concentrate a semi-purified sulfur, and melting and filtering said semi-purified sulfur to produce a sulfur of 99-100% purity.

10. A method according to claim 9 in which the steam is injected at a pressure of 20-50 lbs. per square inch gauge.

11. A method according to claim 9 in which the slurry, after cooling but before flotation, is screened to remove lumps of agglomerated sulfur and the lumps so removed are melted and filtered along with the semi-purified sulfur from the flotation concentrate.

12. A method of recovering sulfur from a native sulfur-bearing ore which consists of grinding said ore, during which a portion of its free sulfur is disintegrated into fines, suspending the ground ore in water along with filter cake from the process to form a slurry of about 20-50% solids, heating said slurry for a period of from 0.25 to 5 minutes with agitation to a temperature above the melting point of sulfur to cause said fines to coalesce, cooling the slurry to a temperature within the range of about 60-90° C. and subjecting it at normal flotation pulp density to a rougher flotation at this temperature and discarding the tailings therefrom, subjecting the concentrate from said rougher flotation to a cleaner flotation at about the same temperature and dewatering, melting and filtering the cleaner concentrate therefrom to produce a sulfur of 99-100% purity, and returning filter cake from said filtering step to said slurring step for reworking.

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EDWARD S. ROBERTS.
SAMUEL STREIZOFF.

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