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December 2, 1955

Mr. John B. Myers, Vice President
Zonolite Company
Libby, Montana

My dear Mr. Myers:

At your request I made a brief visit to Libby to study your milling operations. This visit, in turn, suggested that a day at the Company's Research Laboratory in Evanston, Ill., would be profitable. In the following pages will be found my observations regarding the properties of vermiculite, the ore, the actual mining and milling operations, as well as some suggestions for alternative means for exploiting and concentrating ores. This report is concluded with some specific recommendations (p. 14).

VERMICULITE

The Libby vermiculite is a mineral of the mica family. Like other mica minerals such as muscovite and biotite it occurs in sheets of great lateral extent and minute thickness. The sheets are composed of tightly knit groups of atoms of silicon, aluminum, oxygen, iron and magnesium, arranged in a pattern that is now well understood. The connection between sheets is different in vermiculite on the one hand and ordinary micas on the other. It is on this difference that your Company depends for its existence.

In muscovite and biotite the sheets are negatively charged and this is compensated by positively charged potassium atoms. These ions are anhydrous. The spacing of the sheets is such that the structure repeats itself approximately every 10.2 Angstrom units (one Angstrom unit is approximately one two hundred and fifty millionths of an inch). Of this spacing a very minor part only is due to the potassium, which seems to fit almost exactly into recesses in the atoms of the sheets.

In "true" vermiculite the sheets are likewise negatively charged, and this is compensated by positively charged calcium and magnesium ions. These

ions are half as numerous as the equivalent potassiums of other micas, and considerably smaller in size; one might therefore expect the spacing of sheets to be less than 10A. Actually, however, it is about 14 to 15A, that is about 4 to 5A wider than in muscovite or biotite. This increase in lattice spacing is accompanied by water molecules which populate the space between the sheets.

I share the view of Walker[8] that the magnesium and calcium ions in vermiculite are not anhydrous, but hydrated, for example $[Mg(6H_2O)]^{++}$, these hydrated complexes being much larger than the anhydrous potassium ions (Figure 1). It is well known to physical chemists that the smaller the ion and the higher its charge, the greater the probability of its being hydrated. Since Mg^{++} is about 1.2 A less in diameter than K^+, and since water is about 2.7 A in diameter, $[Mg(6H_2O)]^{++}$ should be about 4.2 A greater in diameter than K^+. The same is also true of hydrated calcium ion ($Ca(6H_2O)^{++}$ should exceed K^+ by about 4.9 A). Thus, replacement of anhydrous potassium by a polyhydrated cation should increase the spacing in mica by about 4 to 5A.

Naturally if the spacing between sheets is increased by 4 to 5A, it becomes much larger than water molecules, which then can move freely in the interplanar spaces. This should provide opportunity for adsorption of water to the atoms of either or both of the adjacent layers. Furthermore the spaces might be wide enough to permit the entrance and adsorption on adjacent layers of additional ions, especially from solutions of high ionic strength. This is in accord with the findings of Doctors Ziegler and Hayes at Evanston.

On heating to a relatively low temperature the adsorbed interlayer water becomes gradually desorbed and it is emitted as steam. At a more elevated temperature the complex hydrated cations suddenly become dissociated; this provides steam, causing the well-known expansion of vermiculite.

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[8] G. F. Walker, Vermiculite and some related mixed-layer minerals, in "X-ray identification and structure of the clay minerals", Chapter VII, pp. 199-223, Mineralogical Society of Great Britain Monograph (1951).

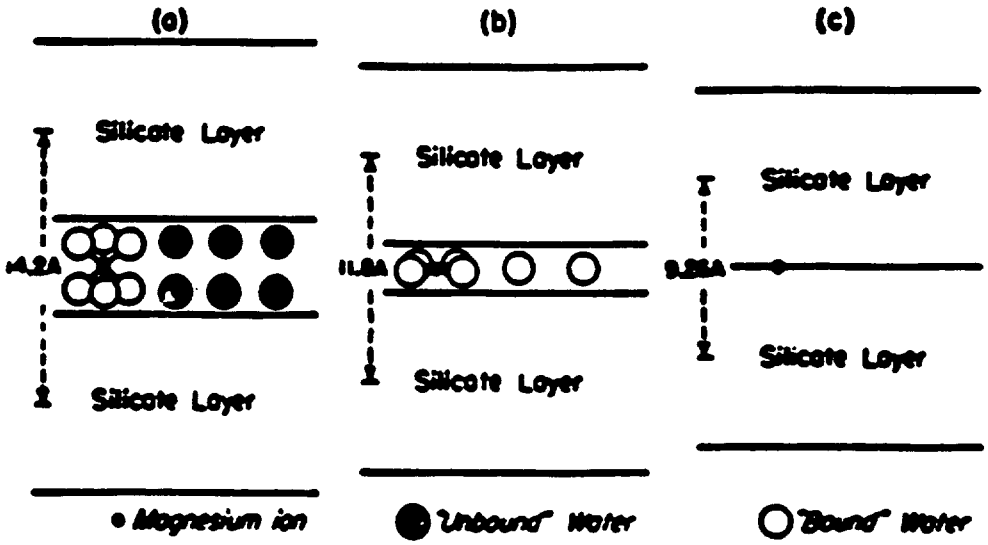

FIG. 1[illegible]. Configuration of the interlayer water in vermiculite (diagrammatic, from Walker.[60] (a) Fully hydrated. (b) About half hydrated after removal of the unbound water. Of the six water molecules in the original hydration shell of magnesium (see a), only four are now in actual contact with the ion. (c) Fully dehydrated with magnesiums in holes in the silicate layers.

On the basis of this picture the only difference between biotite and vermiculite is that between anhydrous potassium on the one hand and hydrated cations plus free water on the other.

In many parts of the mine there occur rather spectacular pieces of ore spangled with coarse mica crystals. The operators refer to this material as biotite, while the more disseminated and crumbly stuff is thought to contain the vermiculite. I am not convinced that such a classification is correct. If you had two distinct minerals, biotite on the one hand and vermiculite on the other, the systematic assay for potassium which is present in one and absent in the other should be diagnostic. As I was saying to you in Libby this can be done readily in a routine fashion by a flame photometer or on the basis of the gamma radiation of potassium. It seems rather likely to me that vermiculite arose from biotite by replacement, but no evidence has been offered to show that the replacement is complete in some places and has not occured in others. I shall therefore assume this replacement to have occured in a random or statistical fashion on a micro scale, and at the same time somewhat more extensively in certain macroscopic areas adjoining cracks and crevices, and less extensively where the crystals were initially coarser and sounder, or where thick "books" of elemental crystals occur in place of thin "pamphlets". In this view there is no sharp demarcation between biotite and vermiculite, but rather all possible gradations. It is because the Libby mineral seems to have retained some potassium that Gruner described it as hydrobiotite, thereby focussing attention on the insertion of water rather then on the replacement of potassium by a hydrated cation.

It might be worthwhile to correlate the useful properties of vermiculite with its potassium content. It might also be useful to seek to extend the replacement made by nature by reacting vermiculite with aqueous solutions e.g. of calcium chloride or of magnesium sulfate. This reaction could be studied not only in the cold, but also at elevated temperatures including temperatures obtainable only in autoclaves. My thought is that if the "biotite" mineral can be reduced in potassium content the yield of the mine could be increased and a product of higher quality made. Furthermore, should such a study prove fruitful tailor-made vermiculites for various [illegible] could be envisaged, and the mine production might include a larger

proportion of the more valuable coarse flake.

The expansion of vermiculite on heating, together with reduction of the lattice dimension normal to the mica sheets with some warping or crinkling in the sheets, is easy to rationalize as a consequence of the randomness of replacement of anhydrous potassium by hydrated calcium and magnesium. At low temperature the adsorbed water is emitted. This reduces locally the thickness of the interlayer space; then dissociation of the aquo-complex ions, which occurs at higher temperatures creates water molecules free to move in the vapor state, and with no place to go. This steam is pinned in some interlayer space by the potassium "rivets" which surround it while new bonds are formed between the anhydrous cations and oxygen atoms in the neighboring layers. Eventually this trapped steam escapes, but by that time the vermiculite is permanently deformed to the expanded state.

This suggests that it would be of value to probe into the scale of the randomness of replacement of which I spoke. Some work is already being done in that direction by electron microscopy. The development of additional techniques would be welcome, for example the examination by electron microscopy of replicas of expanded vermiculite both parallel and at right angles to the basal plane.

Doctor Hayes mentioned to me that swelling of the vermiculite could be obtained by soaking the mineral in the unexpanded form first in strong saline solutions, then in water. For solutions of lithium, sodium, aluminum, calcium and magnesium (all with hydrated cations) there is an increase in volume of up to five or more fold. At the same time the vermiculite takes on a silvery or golden color reminiscent of the color it acquires after thermal expansion. It is not known whether the "swelling" is due to an exfoliation or to a true interlayer swelling or to both. I have suggested experiments to probe into this aspect of the swelling process. I also believe that the swelling property can be used as a basis for an ore-concentration process. Memorandum No. 1 attached to this report outlines the concept of this process.

It has been reported in the technical literature that vermiculite can be expanded not only thermally, but also by soaking it in a concentrated solution of hydrogen peroxide. As this intrigued me I had Dr. Hayes make a simple demonstration of this phenomenon. It then occured to me that some

modifications should be explored so as to find out whether this process can be made useful. A suggestion to this end is offered in memorandum No. 2 attached to this report.

THE ORE

The ore consists of the more or less biotitic vermiculite described at length in the preceding section mixed with an asbestos mineral, pyroxene and portions of igneous rock, moderately coarse in crystallization and of a composition approaching syenite.

The vermiculite occurs in coarsely crystallized masses with flakes up to one inch or more across. Some of these masses up to the size of a desk or larger appear very high grade indeed. They are fragile, breaking readily at grain boundary except when frozen after becoming water-logged. The vermiculite also occurs in finer intergrowth with the asbestos and the pyroxene. The flakes then seem to range from 1/16 inch up to 1/2 inch across, and are thinner than in the other variety.

The asbestos mineral does not seem to be of the kind that has proved so useful and profitable elsewhere. It is pale bluish gray in color, fragile and brittle. In general it occurs as more or less felted clusters characteristically 1/4 to 3/4 inch across. Up to now it has been an unmitigated nuisance; some attention may perhaps be given to find out whether it can be made into a useful byproduct.

The pyroxene breaks readily in sand-size particles often of apple-green color when viewed under water.

The syenite breaks in blocky fashion readily remaining as pieces of rock rather than as pure mineral grains. Occasionally it gives rise to free quartz and feldspar. There is also a little vein quartz in the ore occasionally containing minor quantities of more or less oxidized sulfides, e.g. pyrite.

In specific gravity the minerals offer very little range. The vermiculite is the lightest (2.3 to 2.7), the asbestos is but very slightly heavier (2.35 to 2.95), the syenite quartz and feldspar are all in the range [illegible] to 2.7 also. The pyroxene is slightly heavier being generally heavier [illegible] 2.95. The range offered by the various minerals and their overlap makes [illegible] gravity separation so difficult that it could fairly be described as

futile.

Fortunately the minerals differ in both size and shape. Vermiculite is both the coarsest and flattest. This helps greatly. Mixtures of vermiculite and other minerals also can be made to behave differently when crushed in machines such as rolls in which control is exercised in regard to the nearest approach of the crushing surfaces. These phenomena are utilized in the earlier or dry mill and in the newer or wet mill.

Up to now no use has been made at the Libby mill of differences in wettability between vermiculite and gangue. Differences in wettability in an environment controlled by chemical reagents is at the basis of both flotation and agglomeration. These are currently the most widely-used ore treatment processes. They have been so successful because of their extraordinary flexibility in reducing the specific gravity of one or another mineral in almost any ore mixture. Flotation is suitable for particles finer than 0.01 to 0.02 inch and is therefore not useful for the beneficiation of vermiculite. But agglomeration which can be used for particles up to 1/8 inch in size, or even somewhat coarser, could profitably play a large part in your Libby operations. I will revert to this topic later in the report.

Other possibilities which do not seem to have been explored sufficiently are electrostatic separation and dry magnetic separation. But as these processes may require extraordinarily dry solids they not only may be too expensive, but also objectionable in view of the ulterior processing of the vermiculite. Further inquiry is desirable but it should be given low priority.

Finally some attention might be given to the thought of reducing by swelling the specific gravity of vermiculite so as to facilitate its gravity separation. This is the topic presented in one of the memoranda attached to this report.

THE CURRENT OPERATIONS

Figure 2 is a block diagram of the current operations. This is very highly condensed from an actual flowsheet and designed to bring out the vermiculite discards.

First there is the large tonnage discarded at the mine. The composition of this discard is unknown. When completed a sampling project now in course

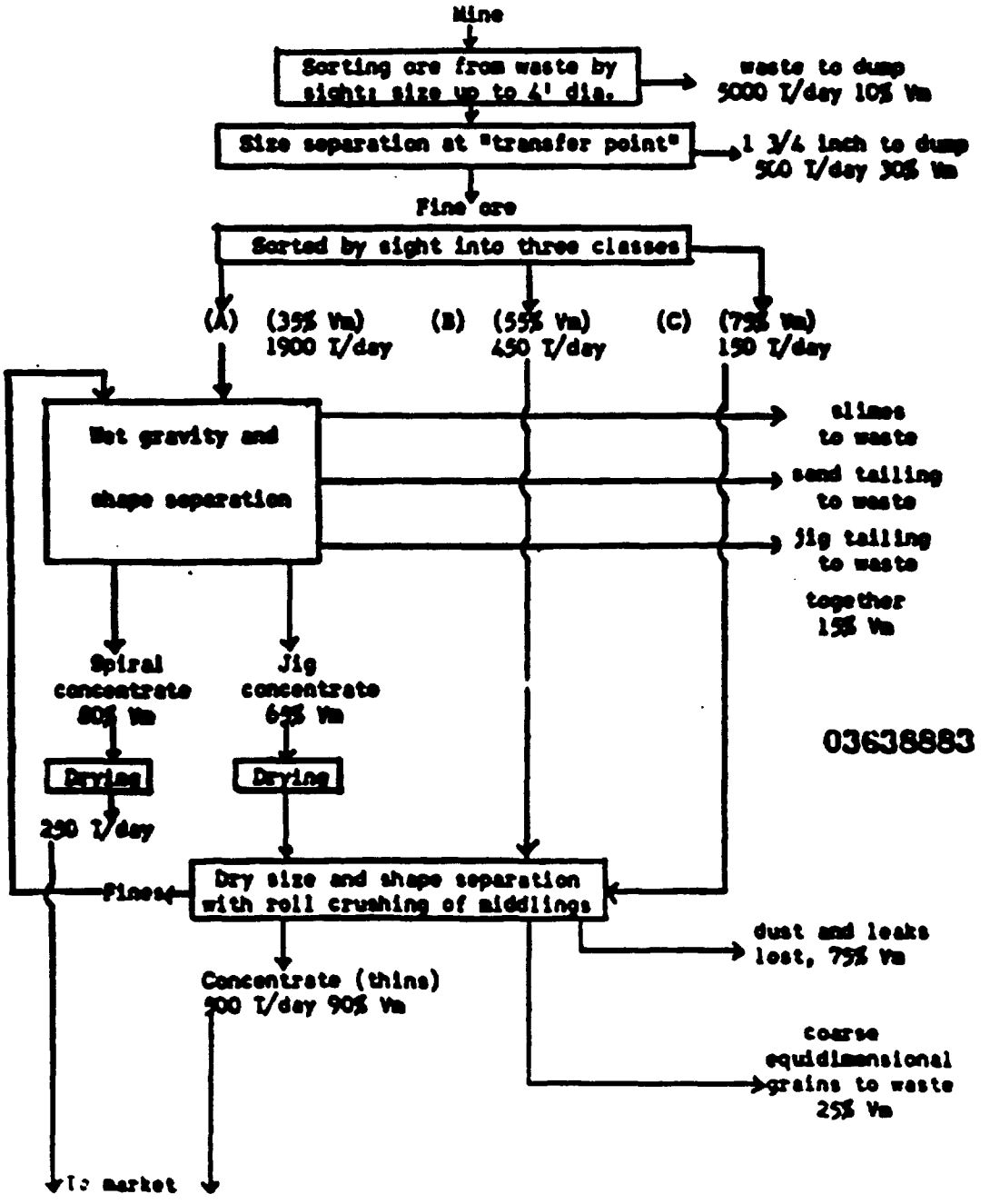

FIGURE 2

Block Diagram of Current Milling Operations
(with approximate tonnages and estimated grades)

should help; but it would be unrealistic to expect too much from it because of the extreme difficulty of sampling truck loads in which the ore particles range in size from several feet to dust and mud. Possibly this large volume of rock would contain on the order of 10 per cent vermiculite. In other words perhaps two thirds as much vermiculite (500T/day) is discarded here as is marketed (750T/day).

Secondly there is the modest tonnage discarded at the transfer point. This was observed to be extremely high on one occasion when high grade (C) ore was being transferred, and to be moderately high when low grade ore (A) was transferred. My impression (which may be faulty if frozen ore was abundant on the occasion of my two inspections of the transfer point) is that the discard at this point is not much lower in grade than the feed accepted by the mill; I suppose it may contain 30% Vm, or 150 tons of vermiculite per day.

Lumping the 1750 tons of the various mill discards at 20% Vm suggests a vermiculite loss in tailings of 350 tons per day. In sum the vermiculite distribution would seem to be of the following order:

In concentrates		750 tons per day
In rock waste	500 tons/day	
In coarse discard	150	
In mill tailings and mill losses	350	
Total losses	1,000 tons/day	

Since the concentrates are only about 85% pure the net vermiculite recovery rock-face to shipments is of the order of 650 tons out of 1650 or about 40 per cent.

Admittedly these estimates are crude. Some improvement in our information is certainly obtainable for most of the mill losses, but mine-loss information will be difficultly obtainable. Furthermore this would be rather academic with the presently-used concentration processes.

The concentration process outlined by Figure 2 is extraordinary in that there is practically no breaking, crushing, or grinding of ore. This procedure was adopted to prevent the degradation in size of the fragile

vermiculite. On the other hand since the separation processes are not very positive much running around of intermediate products is necessary and appreciable degradation does occur, even if it has gone unmeasured. This is suggested by the fact that jig concentrate particles are frequently ragged at the edges while the particles of the same size in the final product are often rounded.

One of the objections to the present flowsheet is that locked particles of which the constituents are moderately tightly bonded to each other remain locked, hence lost in tailings, or a source of off-quality concentrates.

Another of the objections is that the most effective gravity-concentration method for coarse particles (heavy-media separation) is not in actual plant use. It may be that the jigs actually used are the best type of jig, utilizing advantageously the flat shape of the vermiculite. But it seems more than likely to me that a careful mill comparison of heavy-media separation with jigs would show the former to be definitely superior. The experiments now in course should certainly be continued.

Mr. J. B. Calkins has made a pilot-mill comparison between jigging and heavy-media separation, using a small cone-shaped separator. He found a clear advantage for the heavy-media operation. The larger-scale pilot now located in the mill, which uses a drum instead of a cone as separating vessel does not show as much advantage, the thick books of vermiculite, especially, being lost in the tailing. I watched that plant in operation. Mr. Calkins believes its unsatisfactory performance may be due to the low range in gravity of the suspension in the drum (between bottom and top) as compared with the range obtained in the cone. Possibly that is partly the reason for the poor current results, although I suspect other factors may also be involved, e.g. the fact that in the drum the "heavies" are drawn through a layer of "lights" possibly entrapping some of the latter. Also, the ore may have been different, with larger proportion of the thick-book vermiculite when the drum plant was used. Comparison of the drum with the cone (now on order) is clearly desirable. The comparison should be made so as to eliminate the ore and the medium density as variables. I suggested to Mr. Calkins to test the series use of heavy-media drums. We made a short inconclusive run. The matter is worthy of additional study.

I have not liked the dry mill. This may be merely an expression of my own dislike of the dustiness of dry mills. In this case, however, conditions seem so bad that I would rate the operation a temptation to its operators to stay away from the machines entrusted to them. It may even be a serious health hazard. The dust losses and heaping piles of concentrate spill are witness of the inability to practice good housekeeping without excessive cost, —or maybe even with excessive cost. Finally, the multiplicity of units justifies the desire to seek a simpler and more direct processing plant.

ALTERNATIVE CONCENTRATING PROCESS

In Figure 3 I have sketched a flowsheet which I believe capable of substantially increasing the production of vermiculite from the tonnage of ore that is now processed. A number of points raised by this proposal require study. These are the object of the next section in this report.

This flowsheet involves the following features:

1) lesser discard to the mine dump,
2) insertion of a crushing plant, thus eliminating the present discard at the transfer point,
3) all-wet concentrating mill with no segregation of ore types,
4) discard of slimes by screen-size control rather than by classification,
5) heavy-media separation of the coarse sizes (say about + 6 - mesh),
6) agglomeration concentration of the 6 to 35-mesh ore, possibly in two size cuts,
7) wet size-shape cleaning of the heavy-media concentrate,
8) wet roll crushing of the middling from size-shape separation,
9) dry size grading for market sizes.

It is hoped that such a flowsheet should be able to produce about 1100 tons of net vermiculite (in about 1200 tons of concentrate) from the same 8000 tons of ore instead of about 650 tons of net vermiculite (in about 750 tons of concentrate). These figures at present are estimates based on opinion rather than fact, and although I believe them to be realizable, they must of necessity be checked by much experimental work yet to be done.

The nine features of the proposed flow sheet will now be examined in a little more detail.

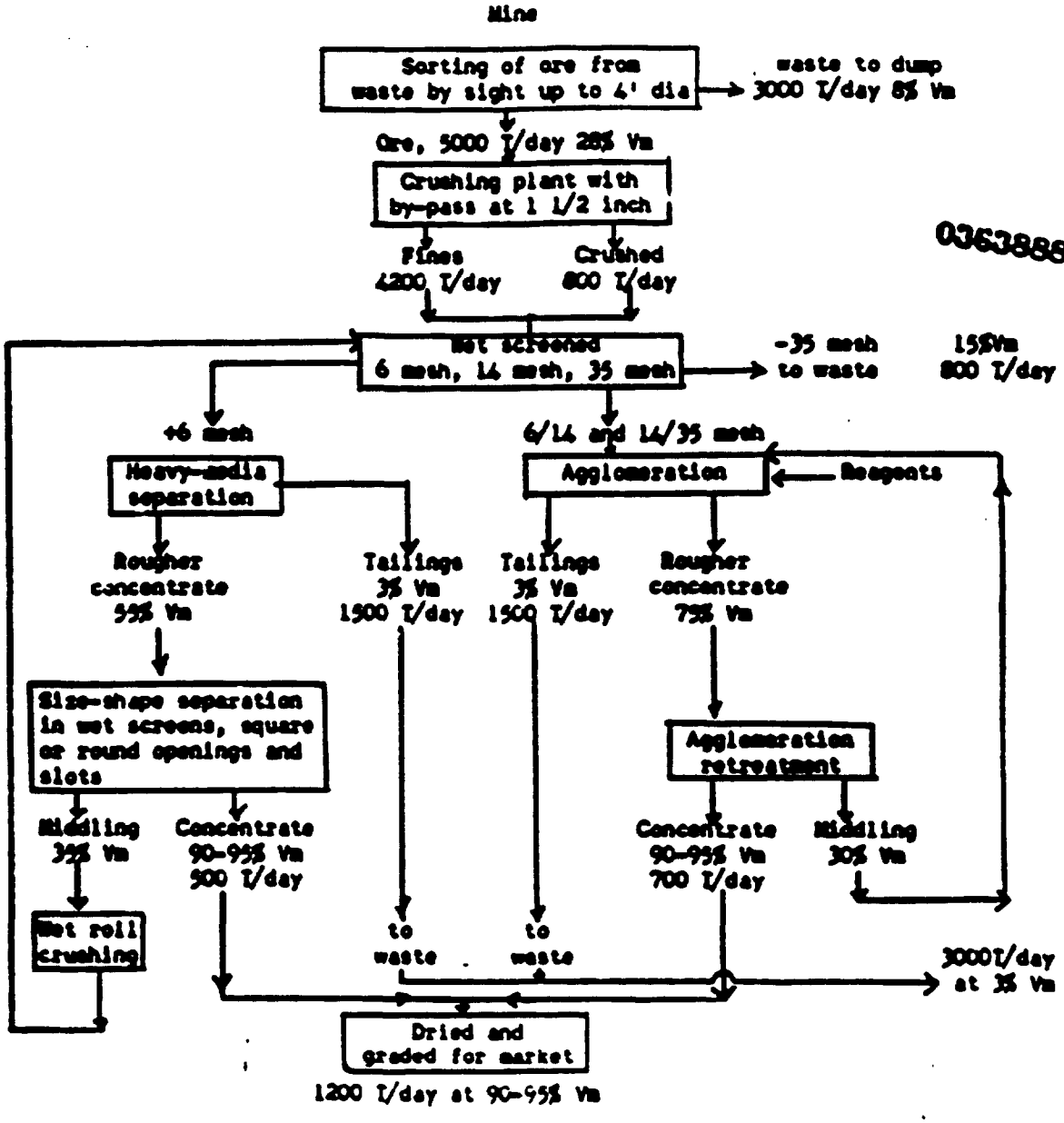

FIGURE 3

Alternative Flowsheet for Libby Ore

Mine dump Much but not all that now goes over the mine dump is coarse syenite. Certainly syenite should continue to go there, but neither low-grade ore nor so-called "biotite ore" should be routed there. The "biotite", especially, should be watched as I fear much very high-grade ore is inadvertently so labeled in the field. The comments in the first section of this report are appropriate in this respect.

Crushing Plant The crushing plant required would consist of a jaw crusher of large gape, followed by a gyratory or cone. Careful weighing of the capital and operating cost of such a plant against the loss in the present transfer-point discard and labor to remove the discard is clearly in order, and it may be that my present hunch that the crushing plant would pay for itself is wrong.

All-wet mill with no ore segregation This is intended to simplify the present multiplicity of ores and plants. It speaks for itself.

Slime discard Because of the flaky character of the vermiculite and of its lesser gravity, classifier control of the discard size is manifestly the wrong way of going about this operating step.

Use of fine wet screens on a large scale is unusual. It may require cooperation with an equipment manufacturer for some development work for a suitable screen operating with the screening surface under water.

Heavy-media separation of coarse sizes This topic has already been discussed in the preceding section. It may be pertinent to add that there is no reason why two or more heavy-media separating cells cannot be used in series in the same fashion that several flotation cells or jigs are used in series to gradually deplete the ore pulp of the desired constituent. Alternatively two heavy-media separations at different gravities may be helpful in producing a final tailing, a concentrate and a middling.

Agglomeration concentration of intermediate sizes Experiments made at Libby several years ago show that extraordinarily good results are realizable. The reagent cost has been thought prohibitively high. But I do not believe that the subject has been appropriately explored. I believe experiments with an anionic collector such as a fatty acid (oleic acid) must not be omitted. To date experiments seem to have been made with cationic reagents in rather wide assortment, but without probing into the relationships of mineral, reagent and aqueous solution. I believe considerable reagent economy is

possible over what has been obtained to date, enough in fact to justify a different conclusion in regard to use of agglomeration at Libby.

Cleaning heavy-media concentrate The heavy-media concentrate would consist of much free vermiculite, some free asbestos, some locked particles of vermiculite, asbestos and pyroxene, and occasional quartz, pyroxene or syenite particles. Size-shape separation in water should work out about as well as in air, and so should roll crushing. No great difficulty is therefore anticipated in adapting these steps at this stage.

If the method of swelling the vermiculite by osmotic pressure does actually swell each particle rather than exfoliate thick books into thin pamphlets, a second heavy-medium separation at lower gravity may do a better job than size-shape separation. In that case swelling followed by a second lower-gravity heavy-media separation would take the place of size-shape separation. In that case also, roll crushing could perhaps be replaced by rod-millgrinding or else the heavies from the second heavy-media separation could go to waste directly.

Wet roll crushing There is no problem here.

Dry size grading for market There is no problem here either.

RECOMMENDATIONS

The unusual properties of vermiculite, which to date are only partly understood suggest the desirability of many researches, so many in fact that some choice must be made as to what should be done first. Among the more important areas of study, I would suggest the following:

1) Increase both absolutely and relatively the effort that is presently being made to understand the mineral vermiculite, and in that connection improve the dissemination of the fundamental knowledge so acquired among those charged with the more utilitarian phases of your work.

2) Improve the knowledge presently available of mine and mill losses.

3) Make a thorough evaluation of heavy-media separation in all its ramifications including pre-swelled ore.

4) Make a thorough evaluation of agglomeration especially directed at a reduction in reagent cost.

5) Study under-water screening as applied to Libby ore.

6) Study the artificial vermiculitization of the more biotitic varieties

of the Libby mineral with a view to improving the quality of the feed to expanding plants.

7) Further study the biotite aspect of the ore, as by systematic potassium analysis.

Very truly yours,

A. M. Gaudin

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Cambridge, Mass.
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