

702 Woodlark Building
Portland, Oregon

No. 4

by

in cooperation with
Oregon State Department of Geology & Mineral Industries



1940

W. H. STRAYER, CHAIRMAN
ALBERT BURCH
E. D. MACNAUGHTON

BAKER
MEDFORD
PORTLAND

EARL K. NIXON
DIRECTOR

PRICE 10 CENTS

FOREWORD

The Oregon State Department of Geology and Mineral Industries, since its establishment in July, 1937, has been well aware that the farmers of the Willamette Valley are greatly handicapped by the high cost of lime fertilizer necessary to neutralize acidity of the soil, as well as to replace the loss of lime caused by drainage.

In 1938 we examined the best-known limestone areas within the valley - the Dallas and Marquam deposits and one or two others - and at that time reached the conclusion that there was little chance of producing high-carbonate stone in the valley at a price that would be attractive to farmers.

During the fall and winter of 1938-1939 we conceived the idea of possibly beneficiating the rock of one or more of the valley deposits. Limestone flotation is not a new process. We proceeded to carry out some preliminary flotation experiments in the Baker Laboratory of the Department. The work was in charge of Leslie L. Motz, staff metallurgical chemist. Mr. Motz was handicapped by lack of both time and facilities but obtained ample data to indicate that there was a reasonable possibility of beneficiating economically the relatively low grade Dallas or Marquam rock and that the test work should be carried to completion.

Fortunately, we were able to make a cooperative arrangement in February of this year with the United States Department of the Interior, Bureau of Mines, for work on various types of Oregon minerals. Representative samples of the Dallas and Marquam limestone deposits were promptly obtained by us and forwarded to the Bureau of Mines laboratory for detailed testing.

Essentially, the answer seems to be that a product running about 85 percent calcium carbonate could be made from the Dallas rock with a metallurgical loss of only 15 percent. First consideration should be given to the Dallas deposit, as it is both larger in tonnage and higher in grade than the Marquam rock. Since our sample of the Dallas rock is said to run about 10 percent in carbonate below the quarry average, it is possible that the above figures could be substantially improved by a commercial plant operation.

Therefore, on the basis of the reasonably favorable flotation results described in the following report, the Department feels justified now in carrying out a further engineering study of the economics of beneficiating the Dallas rock, using assumed production figures that are in line with the reported market demand.

We are pleased to acknowledge our indebtedness to the Bureau of Mines for its part in carrying out the flotation work hereinafter described.

Earl K. Nixon, Director

Portland, Oregon
December 1940

Memorandum

FLOTATION OF OREGON LIMESTONE

by

J. B. Clemmer and B. H. Clemmons*
of the
Bureau of Mines
United States Department of the Interior

This report summarizes the flotation results obtained on samples of limestone from the Dallas and Marquam deposits submitted by the State Department of Geology and Mineral Industries, Portland, Oregon.

The object of the tests was to produce a limestone product suitable for agricultural purposes, from these low-grade materials.

This report supplants a previous memorandum submitted on the Dallas material. Additional tests were made on the Dallas limestone in an attempt to improve the yield of limestone concentrates. These results are included together with the test data on the Marquam sample.

The Dallas and Marquam samples were relatively low-grade and consisted essentially of calcium carbonate associated with shale, quartz, and chalcedonic silica. A head analysis of the samples follows:

	<u>Dallas</u>	<u>Marquam</u>
CaCO ₃	42.6	39.1
MgCO ₃	6.62	4.69
Insol.	39.1	42.0
Fe ₂ O ₃	6.15	8.51
Al ₂ O ₃	5.95	3.15

*Note: The Oregon Department of Geology & Mineral Industries cooperated with the United States Department of the Interior, Bureau of Mines, to the extent of sponsoring the work covered by this report, obtaining and forwarding to the Tuscaloosa Station of the Bureau the limestone samples on which the work was done, and issuing this pamphlet. All credit is due to the Bureau of Mines for carrying out the flotation work described herein, and for preparation of the text of the report.

A microscopic examination of sized portions of the Dallas sample indicated that fine grinding was necessary to liberate the calcium carbonate. Examination of a -200 + 400 mesh portion of the heads crushed to pass 65 mesh showed that about 40 percent of the calcium carbonate was present as clean calcite and the remainder (60 percent) as aggregates containing disseminated shale and silica. Locking of the aggregates persisted below 400 mesh. Minor amounts of plagioclase feldspar, magnetite and chromite were observed in the fine sizes. No discrete grains of magnesite were observed and the magnesia is probably present as dolomite.

The Marquam sample was quite similar to the Dallas except that it was darker and somewhat coarser grained. A microscopic examination of sized products indicated that grinding to 65 mesh was sufficient to free most of the calcium carbonate. This sample contains more iron as magnetite and less shale than the Dallas material.

A representative portion of each of the limestones was stage crushed in rolls to pass 20 mesh and thoroughly mixed. Cut samples of 250 grams each were prepared for flotation by stage grinding in a porcelain pebble mill to avoid excessive sliming of the calcite. The ground charges were floated in a sub-aeration cell of the M.S. type using grind water as the medium. The density was about 25 percent solids.

Sodium carbonate and silicate were used to retard the shale and siliceous materials while floating the limestone with oleic acid or sodium oleate. The froth from the roughing operation was triple-cleaned to give the final concentrates.

No attempt was made in the laboratory tests to use substitutes

for oleic acid. Past experience on other non-sulfides indicates that the tallols, derived from paper-mill black liquors, or the fish oil soaps give results equally as good as oleic acid and are somewhat less expensive. Mr. Motz's report on flotation of the Richlie and Marquam limestone shows that the tallols can be used as a limestone collector.

Several preliminary tests were made on the Dallas material reversing the separation and floating the silica and shale from the limestone with cationic reagents such as duPont 243. The results were inferior to that obtained by flotation of the limestone with soap reagents. Cationic flotation of silica from the limestone does not appear economically feasible. The reagents are too expensive and large amounts are required to affect the separation.

Flotation of Dallas Limestone.

The results of the preliminary tests on the Dallas sample, summarized in a previous memorandum, indicated that acceptable limestone concentrates could be obtained by flotation provided fine grinding was employed. A typical test on a charge stage ground to pass 200 mesh gave concentrates assaying 89.0% CaCO_3 , 5.6% MgCO_3 , 1.3% Al_2O_3 , 1.3% Fe_2O_3 , and 7.6% insoluble. Although such a product should be acceptable for either agricultural purposes or as a cement material, the limestone recovery was low and amounted to only 52.2%. Much of the clean limestone passed into the flotation middlings, indicating the need of a better reagent balance in both the roughing and cleaning operations.

Subsequent tests have given improved results. One of the best tests is recorded in Table No.1. The limestone recovery was 85 percent in a product assaying 84.82% CaCO_3 , 1.45% MgCO_3 , 1.64% Fe_2O_3 , 1.38% Al_2O_3 and 10.7% insoluble. The limestone in the middlings and tailings

was as locked aggregates and could not be recovered without vitiating the concentrate grade.

The improved flotation in this test as compared with preliminary trials can be largely attributed to the use of larger amounts of soda ash in the roughing and cleaning steps. Qualitative tests showed the presence of large amounts of calcium salts in the grind water used in flotation. Since calcium salts are known to adversely affect flotation when using soap reagents their removal is vital for a successful separation. Increasing the soda ash precipitated the lime salts and gave improved flotation.

A test similar to that recorded in Table No.1 was made on a charge stage ground to pass 65 mesh to determine what grade of concentrate might be expected from a coarser grind. About 83 percent of the limestone was recovered in a product assaying 73.6% CaCO_3 , 1.98% MgCO_3 , 2.50% Fe_2O_3 , 2.55% Al_2O_3 , and 19.4% insoluble. The recovery is slightly less than with the finer grind and the concentrates somewhat lower grade. Such a product might, however, be acceptable for agricultural purposes.

Flotation of Marquam Limestone.

The Marquam limestone is coarser grained than the Dallas and is almost completely liberated on grinding to 65 mesh.

A typical test on a charge stage ground to pass 65 mesh and floated in grind water is given in Table No.2. The limestone recovery was 85% in a product assaying 92.0% CaCO_3 , 1.41% MgCO_3 , 1.16% Fe_2O_3 , 0.36% Al_2O_3 , and 3.11% insoluble. Such a concentrate should be suitable for agricultural purposes and no attempt was made to produce a higher grade product.

Other tests on the Marquam sample using less sodium carbonate failed to give a satisfactory separation. The concentrates were low grade and much of the calcite reported in the flotation middlings. Sufficient soda ash to destroy the soluble salts released during grinding is essential for good flotation.

Although 65-mesh grinding gives satisfactory results on the Marquam sample, comparative tests were made on charges stage ground to pass 200 mesh. One of these tests is given in Table No.3. The limestone recovery was about 89% in a product assaying 92.8% CaCO_3 , 1.29% MgCO_3 , 1.32% Fe_2O_3 , 0.15% Al_2O_3 , and 2.66% insoluble. The fine charge floats slower and the concentrates are more difficult to clean than with a more granular grind. The slight gain in recovery or grade of concentrates is insufficient to justify grinding finer than 65-mesh.

Conclusions

The laboratory tests on the Dallas and Marquam samples indicate that a combination of soda ash, sodium silicate and oleic acid in proper proportions enables satisfactory flotation of the limestone in a product of acceptable grade. The tests do not imply, however, that processing of such low grade limestone will be economic.

The Marquam material is more amenable to flotation than the Dallas and may warrant further investigation - should economic factors prove favorable. Pilot plant testing of the Marquam material should precede any attempt at flotation on a commercial scale.

Table No. 1

Flotation of Dallas Limestone ground to pass 200 mesh.

Product	Wt. %	Assay %		% Distribution	
		CaCO ₃	Insol.	CaCO ₃	Insol.
Concentrates	40.9	84.82	10.7	85.0	11.3
Middlings	19.7	17.2	54.6	8.3	27.8
Tailings	<u>39.4</u>	<u>6.9</u>	<u>61.4</u>	<u>6.7</u>	<u>49.3</u>
Composite (Calc.)	100.0	40.80	38.74	100.0	100.0

<u>Reagent</u>					
(Pounds per ton)	<u>Conditioner</u>	<u>Rougher</u>	<u>Cleaner</u>		
			<u>#1</u>	<u>#2</u>	<u>#3</u>
Sodium Carbonate	4.0		1.0	0.5	0.25
Sodium Silicate	0.5		0.5	0.5	0.25
Oleic Acid		0.96			
Time (Min.)	5	5	3	3	2

Table No. 2

Flotation of Marquam Limestone ground to pass 65-mesh.

Product	Wt. %	Assay %		% Distribution	
		CaCO ₃	Insol.	CaCO ₃	Insol.
Concentrates	36.8	92.0	3.1	85.4	2.7
Middlings	8.0	14.4	55.4	2.9	10.6
Tailings	<u>55.2</u>	<u>8.4</u>	<u>65.9</u>	<u>11.7</u>	<u>83.2</u>
Comp. (Calc.)	100.0	39.65	41.96	100.0	100.0

<u>Reagent</u>	<u>Conditioner</u>	<u>Rougher</u>	<u>Cleaner</u>		
<u>(Pounds per ton)</u>			<u>#1</u>	<u>#2</u>	<u>#3</u>
Sodium Carbonate	4.0		1.0	0.5	0.5
Sodium Silicate	0.5		0.5	0.5	0.5
Oleic Acid		0.96			
Time (Min.)	5	5	2	2	2

Table No. 3

Flotation of Marquam Limestone ground to pass 200 mesh.

<u>Product</u>	<u>Wt. %</u>	<u>Assay %</u>		<u>% Distribution</u>	
		<u>CaCO₃</u>	<u>Insol.</u>	<u>CaCO₃</u>	<u>Insol.</u>
Concentrates	37.8	92.8	2.7	88.7	2.4
Middlings	10.9	11.0	60.2	3.0	15.6
Tailings	<u>51.3</u>	<u>6.4</u>	<u>67.3</u>	<u>8.3</u>	<u>72.0</u>
Composite (Calc.)	100.0	39.54	42.07	100.0	100.0

<u>Reagent</u>	<u>Conditioner</u>	<u>Rougher</u>	<u>Cleaner</u>		
<u>(Pounds per ton)</u>			<u>#1</u>	<u>#2</u>	<u>#3</u>
Sodium Carbonate	4.0		1.0	0.5	0.5
Sodium Silicate	0.5		0.5	0.5	0.5
Oleic Acid		0.96			
Time (Min.)	5	5	3	3	3