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Recovery of Silicon Carbide
From Granite Sludge



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Recovery of Silicon Carbide From Granite Sludge

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RECOVERY OF SILICON CARBIDE FROM GRANITE SLUDGE

by

T. O. Llewellyn,¹ G. V. Sullivan,² and E. Martin³

ABSTRACT

The Bureau of Mines conducted laboratory batch beneficiation tests on a waste granite sludge from New Hampshire to determine the feasibility of recovering a reusable silicon carbide product. The granite sludge responded to attrition scrubbing, desliming, and flotation in either alkaline or acid circuits using fatty acid as a collector. Recovery of over 80 percent of the contained silicon carbide at grades of up to 96 percent SiC was obtained.

INTRODUCTION

Silicon carbide (SiC), often known by its trade name of Carborundum,⁴ is a synthetic compound which is commercially produced by heating a mixture of metallurgical coke and high-purity silica sand to a temperature of 2,400° C in an electrical resistance furnace. A method to produce silicon carbide was first discovered in this country by E. G. Acheson in 1891 while studying the reaction of carbon with other materials. The first patent on SiC was issued to him in 1893 (5-6).⁵ The principal producers of silicon carbide are the United States, Canada, France, Switzerland, Italy, Norway, and Germany.

The manufacturing of silicon carbide requires a considerable amount of electrical energy. Some estimates indicate that to produce 1 pound of the material the necessary energy requirement will range from 3.5 to 5 kilowatt-hours (1, 3). The electrical energy required represents over 90 percent of the production cost. The price of minus 8- plus 220-mesh abrasive-grade silicon carbide ranged from \$500 to \$600 per ton in September 1974 (4). There are no set prices, and in most cases negotiations between consumers and producers are required to establish a price.

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⁴Trade names are used for identification only and endorsement by the Bureau of Mines is not implied.

⁵Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

The appearance of silicon carbide varies according to its impurity content. Silicon carbide abrasives usually range from light green (plus 99.5 percent SiC) to black (97 to 98 percent SiC) in color. As impurity content increases (95 to 97 percent SiC), the color usually becomes a black-gray. The green variety is usually harder while the black variety is tougher.

Silicon carbide is used extensively in the dimension stone industry. Fine silicon carbide can be used as a polishing agent for marble and granite. It is also used as grain in wire sawing. The wire saw is a machine designed to cut stone that is considered too large to be cut by circular saws or similar equipment. Hence, wire saws are particularly used in the granite dimension stone industry. A wire saw can be described as similar to a bandsaw except that a twisted wire from 3/16 to 1/4 inch in diameter acts as the band, while silicon carbide particles suspended in water are dragged between the wire and the stone to do the actual cutting (2). The silicon carbide particle sizes most commonly used for wire sawing are mesh sizes minus 30 plus 60, minus 46 plus 70, minus 46 plus 100, minus 60 plus 90, and minus 60 plus 120 (2). Coarse silicon carbide (plus 120-mesh) can be reclaimed by either a cyclone or by gravity means and recycled. The discarded fine waste product is considered a potential, and in some cases a real, water pollution problem. A flotation method for recovery of waste silicon carbide by flotation utilizing fuel oil or creosote as the collector was patented by Watson and Glasser (7). The Bureau of Mines initiated this investigation to determine if an improved flotation process could be developed to process waste silicon carbide sludge that included both coarse and fine material. This study had a dual objective, to reduce the amount of material to be discarded and to recover a valuable product that would provide an economic inducement to treat waste sludge.

ACKNOWLEDGMENTS

The authors wish to thank the Baretto Granite Co., Milford, N.H., for furnishing the sludge sample. W. R. Barton, Bureau of Mines Liaison Officer--Connecticut, Massachusetts, New Hampshire, Rhode Island, and Vermont, for his assistance in obtaining the waste material and furnishing background on the magnitude of the problem. Special recognition is given to Charles E. Spruiell, Jr., physical science technician, Federal Bureau of Mines, Tuscaloosa Metallurgy Research Laboratory, Tuscaloosa, Ala., who developed a rapid method for analyzing the silicon carbide test products.

DESCRIPTION OF THE SAMPLE

A sample of waste granite sludge was obtained by the Baretto Granite Co., Milford, N.H., from an old sludge pond for the study. Chemical analysis showed the material to contain 77.1 percent SiC. In view of the problems occasionally encountered in decomposing silicon carbide for carbon determination, a rapid method for its evaluation was devised. This rapid method is included in the appendix.

The as-received material was a mixture of fine particles and small agglomerates cemented with iron oxide. Microscopic examination of sized fractions of the material after attrition scrubbing and washing showed that the

principal constituent was silicon carbide with lesser amounts of biotite, muscovite, quartz, and feldspar. The sample also contained some opaque minerals and organic material. Silicon carbide analysis of screened fractions are given in table 1.

TABLE 1. - Screen and SiC analysis of Baretto granite sludge

Size fraction, mesh	Weight-percent	Analysis, percent SiC	Distribution, percent SiC
Minus 48 plus 100.....	4.9	90.1	5.7
Minus 100 plus 150.....	22.3	90.3	25.9
Minus 150 plus 200.....	28.4	87.7	32.0
Minus 200 plus 270.....	17.1	76.4	16.8
Minus 270 plus 400.....	13.3	66.7	11.4
Minus 400 plus 20 μ m.....	10.6	50.9	6.9
Minus 20 μ m.....	3.4	30.7	1.3
Composite.....	100.0	77.8	100.0
Head.....	-	77.1	-

BENEFICIATION STUDIES

The beneficiation techniques considered for concentrating the silicon carbide in the granite sludge were high-tension electrostatic, gravity, and flotation. Based on the fact that the processes used in granite stone cutting are wet, the use of electrostatic processes were eliminated because it would require drying the material. Gravity techniques were excluded because of the relatively large amount of fine material present. The effort in this investigation, therefore, was directed toward froth flotation which was conducted with 250-gram samples using a Denver flotation cell.

Initial flotation tests showed that slimes and iron oxide surface coating would have to be removed to enhance selectivity. The material was disaggregated, and the particle surfaces were cleaned by attrition scrubbing. Scrubbing in an opposed-pitch, dual-impeller-type Denver scrubber for 10 minutes at 70 percent solids was sufficient to disaggregate the material and provide clean silicon carbide surfaces for flotation. The minus 20- μ m material was removed by sedimentation methods prior to flotation. Silicon carbide analysis and weight distribution of sized material after attrition scrubbing are presented in table 2.

TABLE 2. - Analysis of material after scrubbing and desliming

Product	Weight-percent	Analysis, percent SiC	Distribution, percent SiC
Plus 20 μ m.....	89.9	79.4	94.9
Minus 20 μ m.....	10.1	37.6	5.1
Composite.....	100.0	75.2	100.0

As previously shown in table 1, the as-received sample contained 3.4 weight-percent of minus 20- μ m material. After attrition scrubbing the total

minus 20- μ m fraction increased to 10.1 weight-percent. This fraction, however, only contained 5.1 percent of the total silicon carbide.

Several reagent combinations and techniques were evaluated for the concentration of silicon carbide, including flotation of the gangue minerals, using the plus 20- μ m fraction as flotation feed. A 1:1 mixture of oleic acid and kerosine in a water emulsion proved to be an effective silicon carbide collector in both alkaline and acid circuits.

In the alkaline circuit technique, the deslimed pulp was conditioned for 10 minutes with 1 pound per ton of sodium silicate. Sodium silicate acted as a pulp dispersant and silicate depressant. The pulp was then conditioned for another 10 minutes with 2 pounds per ton of emulsified collector. The silicon carbide concentrated by flotation at pH 9.2. No cleaning or scavenging flotation steps were made. The results of a typical test are shown in table 3.

TABLE 3. - Flotation of Baretto granite sludge in an alkaline circuit

Product	Weight-percent	Analysis, percent SiC	Distribution, percent SiC
Concentrate.....	66.1	93.5	80.7
Tailing.....	27.5	47.2	17.0
Minus 20 μ m (slimes).....	6.4	29.0	2.3
Composite.....	100.0	76.6	100.0

Flotation tests incorporating the same collector combination and conditioning were also made with the major differences that sulfuric acid (1 pound per ton) was used for pH control and silicate depression and that flotation was at pH 4.0. Results of a typical test are shown in table 4.

TABLE 4. - Flotation of Baretto granite sludge in an acid circuit

Product	Weight-percent	Analysis, percent SiC	Distribution, percent SiC
Concentrate.....	66.7	95.7	84.9
Tailing.....	23.2	32.4	10.0
Minus 20 μ m (slimes).....	10.1	37.6	5.1
Composite.....	100.0	75.2	100.0

The data indicate that flotation was effective in both alkaline and acid circuits. Using the alkaline flotation circuit, a concentrate that recovered 81 percent of the silicon carbide at a grade of 93.5 percent was obtained. When using an acid circuit, the concentrate analyzed 95.7 percent SiC at a recovery of 85 percent. Figure 1 shows that the particles of silicon carbide concentrate still have the characteristic angular structure necessary for abrasive applications.

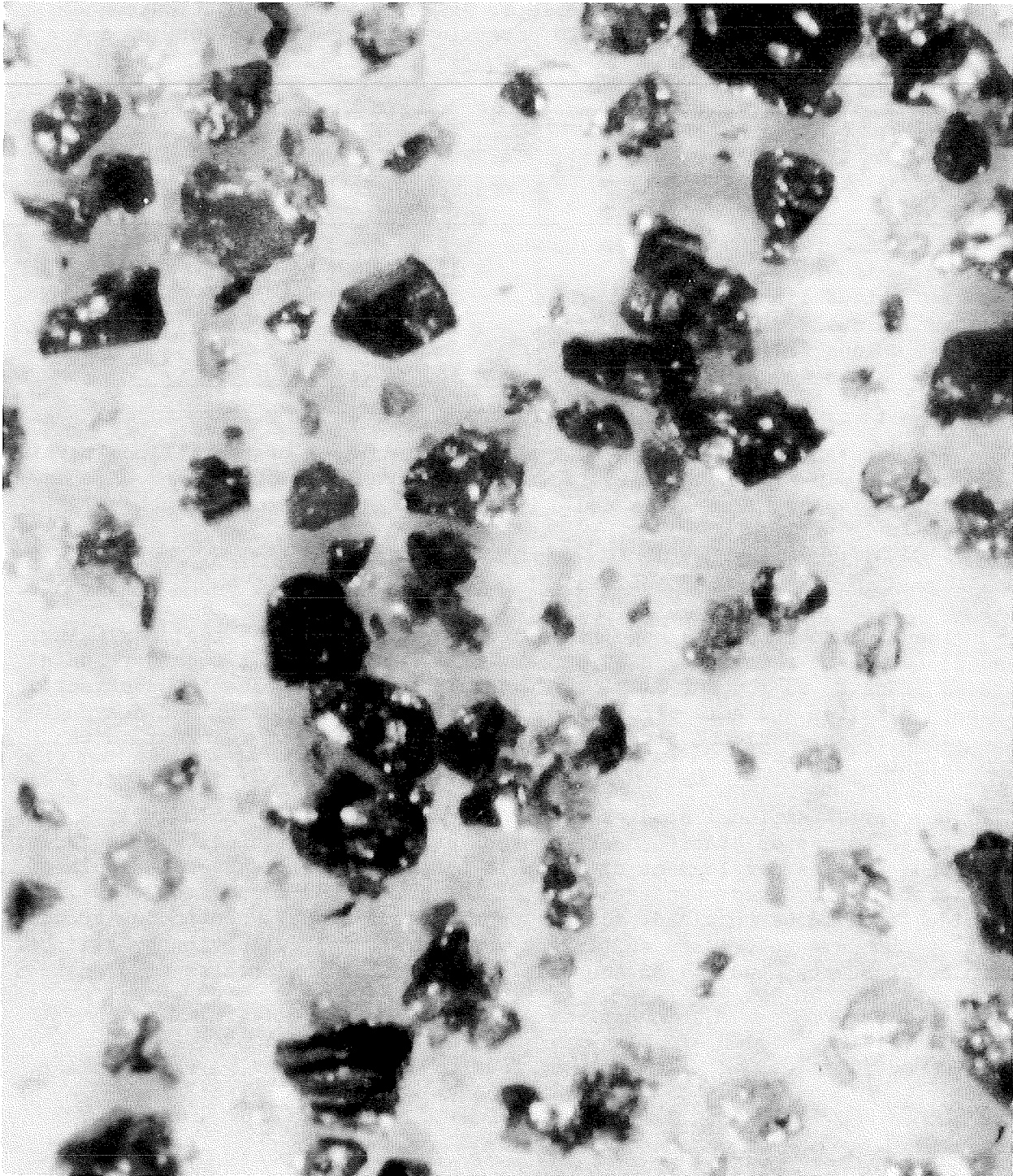


FIGURE 1. - Particle shape of silicon carbide concentrate.

A screen analysis, given in table 5, was made on the flotation concentrate from acid circuit flotation to determine the size distribution of the recovered silicon carbide.

TABLE 5. - Screen analysis of flotation concentrate
(acid circuit)

Size fraction, mesh	Individual weight-percent	Cumulative weight-percent
Minus 48 plus 100.....	5.3	-
Minus 100 plus 150.....	13.6	18.9
Minus 150 plus 200.....	30.5	49.4
Minus 200 plus 270.....	18.6	68.0
Minus 270 plus 400.....	15.6	83.6
Minus 400 plus 20 μ m.....	16.4	100.0
Composite.....	100.0	-

The data in table 5 showed that about 19.0 percent of the silicon carbide is minus 48- plus 150-mesh size. This material can be recycled for wire sawing purposes. The finer sizes could be used for other purposes such as polishing.

CONCLUSIONS AND RECOMMENDATIONS

The Baretto granite sludge responded to attrition scrubbing, desliming, and flotation to recover over 80 percent of the contained silicon carbide at grades of 93 to 95 percent SiC. A single flotation step scheme was effective in both alkaline and acid circuits. Incorporation of cleaning and scavenging flotation steps should be studied to improve SiC grade and recovery in the concentrates.

However, additional studies should be made and should include (1) a comprehensive survey of granite operations to establish the quantity of material involved, (2) the development of a simple scheme that will treat the bulk of the materials involved, and establishment of grades and recoveries of silicon carbide that can be obtained, (3) the operation of a small continuous-process development unit to produce sufficient concentrate for evaluation by silicon carbide consumers, and (4) an economic evaluation of the process or processes developed.

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APPENDIX

A rapid method for evaluating silicon carbide mineral dressing test products from granite cutting and grinding waste fines follows:

Weigh a 1.0000-gram or other appropriate size sample and transfer to a platinum dish. Add 20 ml HF and evaporate to dryness on hotplate. Take up with 20 ml concentrated HCl and evaporate to dryness. Repeat this HF, HCl attack a total of three times. Take up with 10 ml HCl and heat to dissolve soluble salts. Dilute to 50 ml with distilled water and filter using Whatman No. 40 paper or equivalent. Wash five times with hot water. Transfer filter paper and residue to a tared porcelain crucible and burn off paper. Weigh and subtract tare weight. Weight of residue divided by sample weight times 100 equals percent silicon carbide.

It is recommended that periodic microscopic examination of residues be performed to determine that no undecomposed gangue materials remain in the silicon carbide product.

The validity of this determination was proven by treating a sample of 100 grit silicon carbide by the above procedure. The silicon carbide recovery was 99.8 percent.



