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REPORT OF INVESTIGATIONS—NO. 47

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# DECOLORIZATION OF SOUTHERN ILLINOIS SILICA

BY

J. S. MACHIN AND F. V. TOOLEY



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University of Illinois; *Pleistocene Invertebrate Paleontology*,  
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Geological Survey.

This Report is a Contribution of the Section of Geochemistry,  
Frank H. Reed, Chief Chemist.

December 1, 1937

## CONTENTS

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	PAGE
Introduction.....	5
Acknowledgments.....	6
Characteristics of the material.....	6
Decolorization by iron removal.....	7
High temperature methods.....	7
Leaching with acids alone.....	8
Leaching with acids and reducing agents.....	8
Electrical methods.....	9
Magnetic separation of iron oxide.....	9
Bleaching without removing iron.....	9
Choice of methods for Illinois silica.....	9
Factors to be considered.....	9
Consideration of the processes.....	10
Experimental investigations.....	11
Leaching with hydrochloric acid.....	13
Leaching with sulfuric acid.....	17
Metal-bisulfite-acid process.....	20
Application of the metal-bisulfite-acid process.....	30
Recapitulation and Remarks.....	33
Bibliography.....	34

## ILLUSTRATIONS

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### FIGURE

1. Iron removed from silica by treatment with HCl of varying concentration.....	12
2. Iron removed from silica by treatment with boiling HCl for varying times.....	13
3. Iron removed from silica by treatment with HCl at room temperature.....	14
4. Iron removed from silica by treatment with H <sub>2</sub> SO <sub>4</sub> of varying concentration.....	16
5. Iron removed from silica by treatment with boiling H <sub>2</sub> SO <sub>4</sub> for varying times.....	17
6. Iron removed from silica by treatment with H <sub>2</sub> SO <sub>4</sub> at room temperature.....	18
7. Theoretical leaching cycle using HCl or H <sub>2</sub> SO <sub>4</sub> .....	19
8. Iron removed from silica with various mixtures of H <sub>2</sub> SO <sub>4</sub> and NaHSO <sub>3</sub> in the presence of zinc.....	21
9. Acid concentration vs. per cent of total Fe <sub>2</sub> O <sub>3</sub> removed using different ratios of NaHSO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> .....	22
10. Variation of pH with time when silica is leached in the presence of zinc with a mixture of H <sub>2</sub> SO <sub>4</sub> and NaHSO <sub>3</sub> .....	24
11. Decline in efficiency of leach liquors with increasing quantities of silica.....	26
12. Cumulative acid additions necessary to maintain pH.....	27
13. Sulfur precipitation in zinc-H <sub>2</sub> SO <sub>4</sub> -NaHSO <sub>3</sub> water mixtures.....	29
14. Theoretical leaching cycle employing the H <sub>2</sub> SO <sub>4</sub> -NaHSO <sub>3</sub> -metal process.....	32



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# DECOLORIZATION OF SOUTHERN ILLINOIS SILICA

By

J. S. MACHIN AND F. V. TOOLEY

## ABSTRACT

The problem resolves itself into one of iron removal. Possible methods of decolorizing silica are classified roughly as high temperature methods, wet leaching with acids alone or in the presence of reducing agents, electrical or magnetic separation of iron compounds. Factors to be considered in the choice of a method are the capacity of the mills, the cost of applying the process, the degree of iron elimination attained, the health and corrosion problems involved, and the physical characteristics of the silica. Experimental investigations of three wet leaching methods employing first hydrochloric acid, second sulfuric acid, third a combination of an active metal with sodium bisulfite and sulfuric acid, indicate that it is technically feasible to bleach by any of the three methods investigated. Cost factors are considered but reliable estimates are not possible without pilot plant data.

## INTRODUCTION

The U. S. Bureau of Mines "Minerals Yearbook for 1936" classifies southern Illinois silica as tripoli under the general heading Natural Silica Abrasives, although the larger part of the production in Illinois is not used for abrasive purposes. The reported production of tripoli in the United States for the year 1935 was 27,375 short tons valued at \$383,416. Of this total there was reported from Illinois 10,001 tons valued at \$113,484.<sup>1\*</sup>

For 1936 the annual figures list a production of 28,487 tons of tripoli valued at \$391,878. The Missouri-Oklahoma and the Illinois fields were the principal producing areas. Illinois in 1936 produced 10,981 tons valued at \$138,063.<sup>2</sup>

One of the most important outlets for southern Illinois silica or tripoli is through its use as an inert extender in the paint industry. The paint manufacturer is interested in the availability of a steady source of supply of a material that is uniformly white. One way to meet the condition of uniformity in the matter of color would be through decolorization of the silica, controlling the color by removal of colored impurities.

The present practice among the silica producers in southern Illinois is to control the color through selective mining and handsorting of the crude silica after it is shot down.

The advantages which would accrue to the producer from a cheap and efficient decolorization process would appear, first in a product of uniform color, second in the fact that the necessity for selective mining and hand-sorting of the crude silica would be minimized.

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\* See Bibliography, pages 34 and 35.

The objectives of this investigation were: (1) To find among the known methods for bleaching nonmetallic minerals those processes which might give promise of applicability to southern Illinois silica; (2) to obtain sufficient data on such processes to afford some basis for estimation of relative effectiveness and relative costs; and (3) to collect fundamental information which would be of help in the development of an operating cycle for a pilot plant.

#### ACKNOWLEDGMENTS

This investigation was proposed by J. E. Lamar, Geologist, Illinois State Geological Survey and was planned by and assigned to C. F. Fryling, formerly Chemist of the same organization. Under the direction of Dr. Fryling an extensive survey of the literature bearing on the problem was made and considerable preliminary experimental work was carried out. Due to the fact that Dr. Fryling left this organization to take a position with an industrial concern, the project was reassigned to J. S. Machin.

Valuable cooperation was afforded by various members of the staff of the Survey. In particular, thanks are due to Dr. O. W. Rees of the Analytical Division for various analyses carried out under his direction and to Dr. F. H. Reed, Chief Chemist, for valuable suggestions.

#### CHARACTERISTICS OF MATERIAL

The variety of silica under consideration is a porous, nearly white, siliceous rock. The rock is made up of extremely fine crystals and crystal fragments of quartz. There are three general types of aggregation, which grade into each other more or less. The first type is a very friable variety which can be pulverized in the hand. The second type is a phase which offers considerably more resistance to crushing forces but can be cut with some difficulty with a knife. The third type is a hard cherty material which occurs in seams and as random rounded inclusions in the mass of the deposit. The term "amorphous silica" often used to designate this material is misleading. While there are no large crystals, the grains of the finely ground material are shown by microscopic examination to be distinctly crystalline and to exhibit double refraction.

The diffraction pattern produced by passing an X-ray beam through the powdered silica is identical with that produced by ground quartz. The average ultimate particle diameter indicated by these diffraction patterns is  $10^{-4}$  to  $10^{-6}$  millimeters.<sup>3</sup>

The mine run silica is usually 95 per cent or more  $\text{SiO}_2$ . The principle impurities usually reported on analyses are  $\text{Al}_2\text{O}_3$ , 0 to 2.5 per cent;  $\text{Fe}_2\text{O}_3$ ,

0 to 1 per cent; MgO, 0 to 0.3 per cent; CaO, 0 to 0.3 per cent; ignition loss, 0.2 to 1.2 per cent.

The reddish-colored stains which appear irregularly through the mass of the deposits consist mostly if not entirely of oxides or hydrated oxides of iron. These stains appear to have been formed in the deposits by precipitation of iron compounds from the ground water which entered the mass of mineral along cracks and other irregularities of structure. The iron stains are greatly concentrated along the approximately horizontal seams of the more impervious cherty material. The fact that the major portion of the iron can be dissolved out rather easily by acid leaching solutions indicates that little or no silicate iron is present.

The rock has a grayish cast when wet. The cause of this phenomenon is not certainly known. The fact that silica which has been ignited at red heat does not exhibit the gray color lends support to the view that the color is caused by traces of carbonaceous matter. It has been suggested that it may be due to a condition of the silica crystals similar to the condition of sodium chloride crystals which results in so-called blue rock salt.

By far the greatest amount of objectionable color in this rock is due to iron stains. The problem—one which has plagued the users of non-metallic minerals especially in the glass and ceramic industries—is therefore resolved into one of removing the iron compounds or of neutralizing the color due to them.

## DECOLORIZATION BY IRON REMOVAL

### HIGH TEMPERATURE METHODS

There have been described in the literature and in patents various processes for the removal of iron from nonmetallic minerals by means of high temperature operations. High temperature is here interpreted to mean any temperature above that of low pressure steam. These methods may be grouped roughly into three classes.

The first class includes those processes which employ corrosive gases such as phosgene, chlorine, hydrogen chloride, carbon monoxide, etc., singly or in combination. The desired result is accomplished by converting the iron present into volatile compounds which are removed in the gaseous phase. An example of this class is G. A. Hulett's<sup>4</sup> method whereby the dry material, such as sand, at a temperature 300 to 600 degrees centigrade is subjected to the action of phosgene ( $\text{COCl}_2$ ) gas. The iron compounds present are thereby largely converted into volatile compounds, presumably iron carbonyl or ferric chloride or both. These compounds, which are gaseous in the temperature range named, are swept away by the continuous current of phosgene.

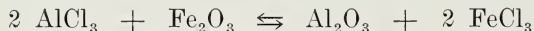
For other representative examples see literature references<sup>5-9</sup> at the end of this report.

The second class differs from the first in that it involves a two-step operation. The first step is a reduction of the iron compounds present to metallic iron, the second step the removal of the iron.

An example is the Vereinigte Stahlwerke process<sup>10</sup> whereby the iron is said to be eliminated from certain crude materials such as kaolin, quartzite, etc. "by first converting the iron oxide contained in these materials into metallic iron by means of reducing gases at elevated temperatures and then converting the metallic iron thus produced into volatile iron pentacarbonyl by treatment with carbon monoxide, the substance under treatment itself in many cases acting as a catalyst."

Other examples of this type are to be found under references 11 and 12.

The third class of high temperature iron removal methods employs a salt—usually a chloride such as basic aluminum chloride—which is mixed with the material from which iron is to be removed. The mixture is then roasted at a temperature high enough to cause volatilization of ferric chloride. A reaction of the type



is depended upon to convert the iron to a volatile and/or soluble form. A part of the iron is volatilized. The high temperature treatment may be followed by lixiviation with water or dilute acid to further reduce the iron content.<sup>13-15</sup>

Some miscellaneous high temperature methods involve combinations somewhat outside the above classification but are of no particular interest in connection with a material such as southern Illinois silica.

#### LEACHING WITH ACIDS ALONE

The use of hydrochloric and sulfuric acids to remove iron stains by simple solution and washing is too well known to require comment.<sup>20, etc.</sup>

#### LEACHING WITH ACIDS AND REDUCING AGENTS

The fact that the rate of solution of ferric oxide in acid solutions is increased in the presence of reducing agents and the explanation usually given in terms of the equilibrium laws are common knowledge. Processes for removing iron stains based on this principle have appeared frequently in the literature. A variety of reducing agents, of which the following is a partial list, have been proposed.

Hydrosulfurous acid and its salts.<sup>17, 18, 19</sup>

Aldehyde sulfoxylic acid and keotone sulfoxylic acid and derivatives of either.<sup>21</sup>



Cuprous salts.<sup>22</sup>

Metals in the presence of sulfurous acid or its salts.<sup>23, 24, 25</sup>

Ferrous sulfate.<sup>26</sup>

Hydrogen sulfide and alkali sulfides.<sup>27, 28</sup>

Oxalic acid and its salts.<sup>29, 30, 31</sup>

Combinations of the above or other reducing agents.<sup>32</sup>

### ELECTRICAL METHODS

Attempts have been made to separate finely divided ferric oxide from suspensions of clay by subjecting the suspension to the action of an electric field. The process depends on the phenomenon known as electrophoresis. Electrically charged, particles in suspension migrate toward the cathode or the anode according to the sign of their charges. Kollman<sup>33</sup> and Ormandy<sup>34</sup> claimed some success with the method. They found that iron and other impurities deposit on the cathode. Other workers, notably Hopkins<sup>35</sup> and Bleininger<sup>36</sup> have not been able to achieve satisfactory iron removal by electrophoresis.

### MAGNETIC SEPARATION OF IRON OXIDE

Until recently the magnetic separator machines built were not suited in design to the removal of comparatively nonmagnetic materials such as iron oxides (except magnetite). It is claimed,<sup>37</sup> however, that recently due to improvements in design and increased intensity of the fields employed in these machines, progress has been made toward the solution of the problem of removal of iron oxides from nonmetallic materials.

Attempts to clean southern Illinois silica on these high intensity magnetic separators have not as yet met with success, probably because of the manner in which the iron is distributed in the silica.

### BLEACHING WITHOUT REMOVING IRON

It has been proposed<sup>38</sup> that yellow tints due to iron be neutralized by treatment with ferrocyanide whereby part of the iron is converted to blue ferric ferrocyanide. The insoluble blue salt is supposed to mask or complement the tint due to oxides of iron. The permanence of the effect seems doubtful except under favorable conditions even if the bleaching were successfully accomplished.

## CHOICE OF METHODS FOR SOUTHERN ILLINOIS SILICA FACTORS TO BE CONSIDERED

*Size of the industry.*—Any process to be economically feasible must not involve the installation of equipment such that the interest and depreciation

charges on such equipment will be out of proportion to the yearly value of the product of the plant.

*Costs.*—The cost of labor, and of fuel and reagents consumed per ton of silica treated must be kept down. The allowable figure will depend on whether the treated product will command a better price and on whether savings can be made in the cost of crude silica where a bleaching process is used.

*Efficiency of a process.*—The word efficiency is used here in a narrow sense to refer to the capacity of the process to reduce the iron content of southern Illinois silica to a low value.

There appears to be no recognized standard expressed in terms of allowable iron. Samples of the material are compared to standard samples which have proved themselves satisfactory in the matter of color by having been accepted by the consuming buyers. Among samples analyzed at the Illinois State Geological Survey one described as of satisfactory color contained 0.04 per cent iron reported as  $\text{Fe}_2\text{O}_3$ , another described as "off color" contained 0.05 per cent iron on the same basis.

*Health hazards.*—The use of gases such as phosgene, carbon monoxide, chlorine, etc. constitutes a health hazard control of which adds to the cost of any process employing such reagents.

*Corrosion problems.*—All of the classes of processes listed above except magnetic separation employ reagents which are corrosive to metals and to wood in greater or less degree. This factor must be taken into consideration in the design of equipment and hence has an important bearing on the cost.

*Physical characteristics of southern Illinois silica.*—It should be kept in mind when considering any wet process that tripoli is an absorbent material. Rough tests have indicated that the substance will retain from 40 to 45 per cent of its weight of water when ground by passing through a roll crusher with rolls set one sixteenth-inch apart, then wetted and the excess water allowed to run off. This would mean that if a ton of this material were treated with, let us say, a 10 per cent solution of hydrochloric acid there would be retained in the silica in the neighborhood of 800 pounds of hydrogen chloride solution which is equivalent to 254 pounds of commercial twenty degree hydrochloric acid.

#### CONSIDERATION OF THE PROCESSES

Any of the high temperature processes would require relatively expensive plant equipment. This is especially true of those which employ gases which are corrosive or poisonous or both. The size of the present day silica industry is not, in the opinion of the authors, consistent with serious consideration of any high temperature process.

Leaching with acids alone is recommended by its apparent simplicity. The iron content of silica may be reduced to low levels by this method. To control the efficiency of iron removal we may vary the acid concentration, the time during which the silica is exposed to the action of the acid solution and the temperature. The corrosion problems, however, become more serious at higher acid concentrations and higher temperatures. This method was considered to be worthy of experimental investigation.

Among the most effective and most rapid methods that we have for dissolving oxides of iron are those employing acids in the presence of reducing agents. In this group therefore is a likely place to search for means of bleaching silica.

A number of the processes listed above under this group were tried in a qualitative fashion, on a badly discolored sample of silica. In most cases there was some bleaching observable. If, however, the sample was not bleached white or nearly so the process was not investigated further. The time required to effect bleaching, the number of operations involved, the original cost of the reagents required, the concentrations at which the reagents were used, the ease or difficulty with which reagents could be reclaimed from used leach liquors, whether or not objectionable gases were evolved and any other pertinent facts were considered in the attempt to determine which processes gave most promise of being suited for use under the conditions existing in the southern Illinois silica mills. On the basis of these preliminary experiments and the considerations referred to it was decided to investigate quantitatively the effect of leaching silica with hydrochloric acid and with sulfuric acid, and to also examine experimentally a process based on the action of a mixture of sodium bisulfite and sulfuric acid while in the presence of an active metal such as iron or zinc. Accounts of these investigations are presented below.

## EXPERIMENTAL INVESTIGATIONS

In all experiments described below the silica samples employed were from a badly stained mass sample containing 0.54 per cent iron reported as  $\text{Fe}_2\text{O}_3$ . The samples for which data are given were ground to pass a 100-mesh screen. While it is not to be expected that equally efficient leaching would be obtained with coarser grinding it has been our experience that, due probably to the porous nature of the mineral, good leaching efficiency can be obtained with comparatively coarse material. Using silica samples which were ground by passing once through a roll crusher with the rolls set approximately one-sixteenth of an inch apart, it has been possible to remove more than 90 per cent of the iron present in the silica by acid leaching and more than 60 per cent by the acid-bisulfite-metal process.

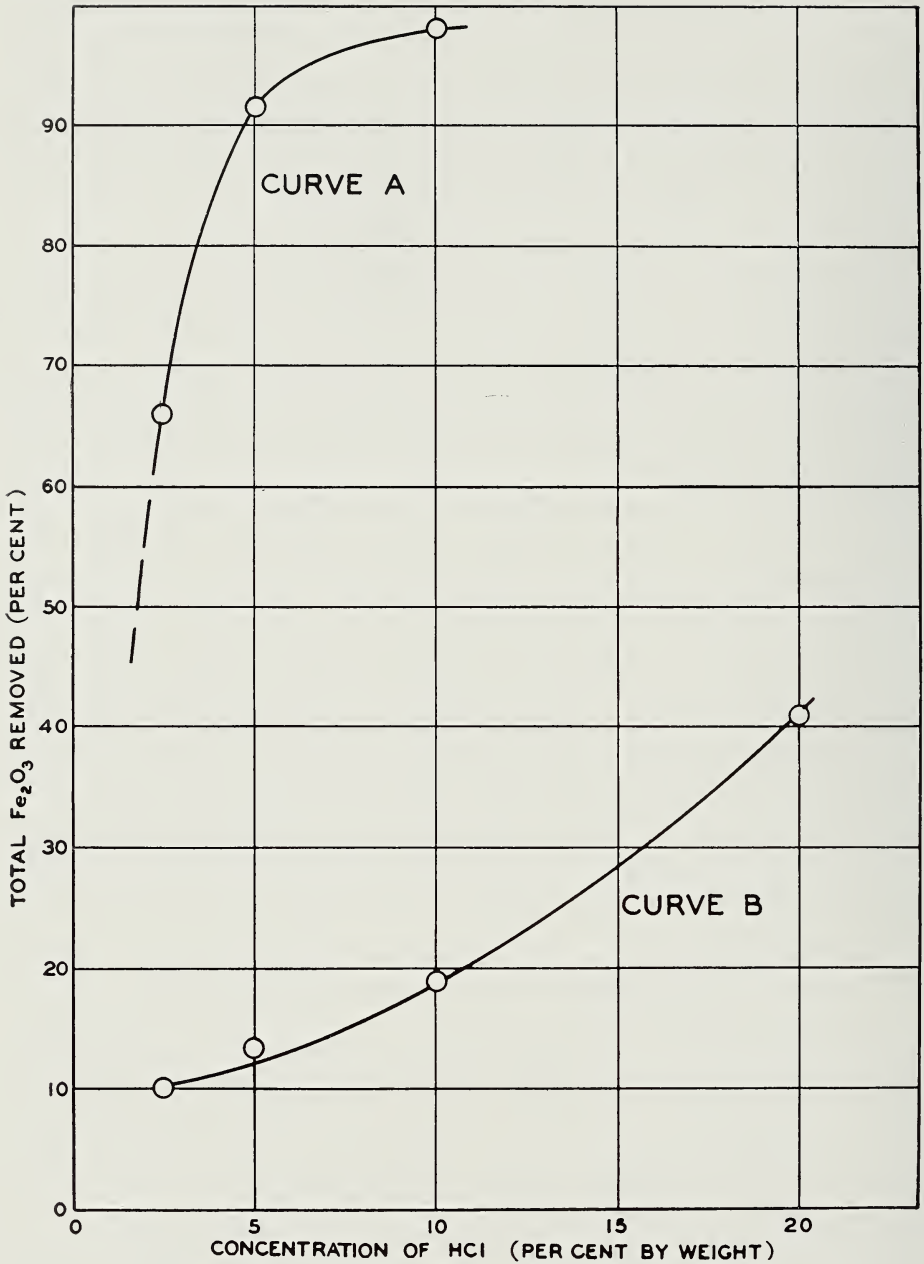


FIGURE 1

Variation in per cent of total iron present in silica which was removed by two hour treatment with hydrochloric acid solutions at boiling temperature (curve A) and at room temperature (curve B).

The per cent of the total iron present in the silica which was removed by leaching was determined in every case by filtering off the leached silica, washing, and analyzing the combined filtrate and washings for iron. The iron was determined by titration with standard ceric sulfate solution following reduction of the iron to the ferrous condition with the silver reductor.

### LEACHING WITH HYDROCHLORIC ACID

The effect of leaching iron-stained silica with hydrochloric acid under some varying conditions of time, temperature, and acid concentration is shown graphically in figures 1, 2, and 3. The data for figure 2, and for curve A, figure 1, were assembled as described in the next paragraph. They are recorded in table 1.

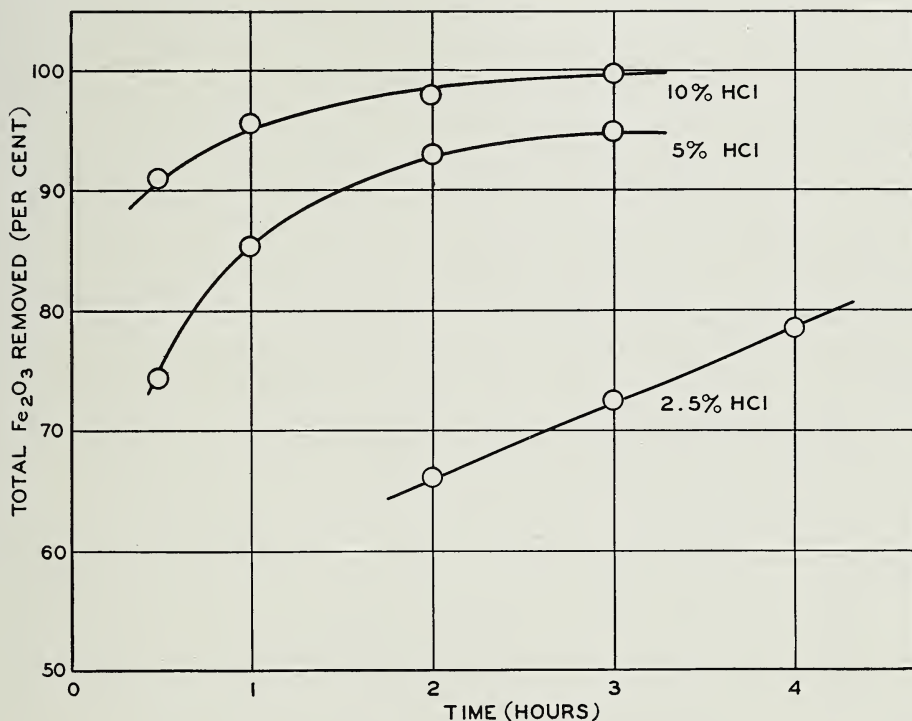


FIGURE 2

Variation in per cent of total iron present in silica which was removed by treatment, at boiling temperature for various periods of time, with hydrochloric acid solutions of the indicated concentrations.

Ten grams of silica were placed together with 25 ml of HCl solution of the desired concentration, in conical flasks of 250 ml capacity. These flasks were connected by means of ground glass joints to long air cooled reflux condensers and heated by means of small bunsen flames so as to boil gently.

The materials for the experiments recorded on figure 1, curve B, were assembled in the same manner as the others. They were shaken occasionally but were not heated. At the end of the leaching period the samples were filtered and the filtrates analyzed for iron.

The solutions were made up from commercial C. P. acid. The manufacturer's figures on its concentration and density were used. The concentrations are expressed in per cent of anhydrous acid by weight.

The data used in figure 3 were obtained as follows: Five gram samples of silica and 12.5 ml of HCl solution of appropriate concentration were placed in test tubes and allowed to stand. All tubes were shaken frequently during the daytime but not at night. The samples and acid were prepared as described above. At the end of the leaching period the samples were filtered, washed and the iron removed was determined after the manner previously described.

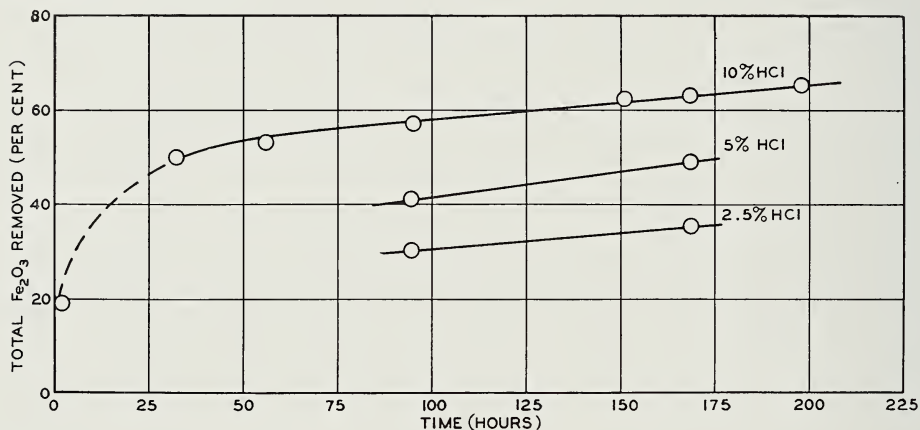


FIGURE 3

Variation in per cent of total iron present in silica which was removed by treatment, at room temperature for various periods of time, with hydrochloric acid at the indicated concentrations.

Advantages of the hydrochloric acid method are: (1) Simplicity of the principle; (2) possibility of removing high percentage of iron; (3) single reagent in leach liquor; and (4) complete removal of acid from the product is easily accomplished because of the volatility of hydrogen chloride.

The disadvantages are: (1) It is necessary to work at or near the boiling temperature to get good iron removal with low acid concentrations. Even at higher concentrations rather long time periods are required at ordinary temperatures. The longer the time period the more leaching tanks would be required for a given quantity of silica treated per unit of time.

(2) The leach liquor and vapors are highly corrosive to metals. Waste liquor and washings might have to be neutralized by discharge on a bed of crushed limestone to avoid nuisance suits.

(3) Reconcentration of the run off or washings would probably be impractical due to their corrosive character and the consequent cost of reconcentration equipment.

(4) The cost of hydrochloric acid (20° Bé.) at the current market (October 1937) is \$22.00 per ton. The cost of decolorizing a ton of silica would depend on many factors, most of which are impossible to estimate in advance of development of an operating cycle on a pilot plant scale. If 10 per cent HCl solution were chosen as the leach, to be used cold and the run off and washings reconcentrated to the original strength it is estimated that the cost of acid and of coal per ton of silica treated would amount to about one dollar. This estimate assumes that 800 pounds of liquid will be retained by one ton of silica crushed to minus ¼ inch. Eight hundred pounds of 10 per cent HCl solution is equivalent to 250 pounds of commercial hydrochloric acid worth \$2.75. The estimate includes cost of fuel to evaporate water, cost of acid residue finally discarded in the washings, and cost of acid actually consumed (0.5 per cent Fe<sub>2</sub>O<sub>3</sub> assumed to be present in the crude silica). No other costs are included in the estimate, because labor, equipment depreciation, and such items depend on factors which cannot be estimated safely until an operating cycle is developed.

TABLE 1.—LEACHING WITH HYDROCHLORIC ACID

Test Number	Acid Concentration (Per cent by Weight)	Leaching Conditions	Leaching Period (Hours)	Fe <sub>2</sub> O <sub>3</sub> Removed (Per cent)
277.....	2.5	Reflux	2	66.6
315.....	2.5	do.	3	72.8
316.....	2.5	do.	4	78.3
331.....	5.0	do.	0.5	74.3
317.....	5.0	do.	1	85.6
332.....	5.0	do.	2	93.0
318.....	5.0	do.	3	94.6
333.....	10.0	do.	0.5	91.1
319.....	10.0	do.	1	95.7
334.....	10.0	do.	2	98.4
320.....	10.0	do.	3	99.4
281.....	2.5	Room temp.	2	10.2
282.....	5.0	do.	2	13.4
283.....	10.0	do.	2	18.6
284.....	20.0	do.	2	41.2
321.....	10.0	do.	32	50.5
322.....	10.0	do.	56	53.6
323.....	10.0	do.	96	56.6
324.....	10.0	do.	151	61.8
325.....	10.0	do.	168	62.7
326.....	10.0	do.	198	64.9
327.....	5.0	do.	96	41.7
328.....	5.0	do.	168	48.8
329.....	2.5	do.	96	30.1
330.....	2.5	do.	168	35.1

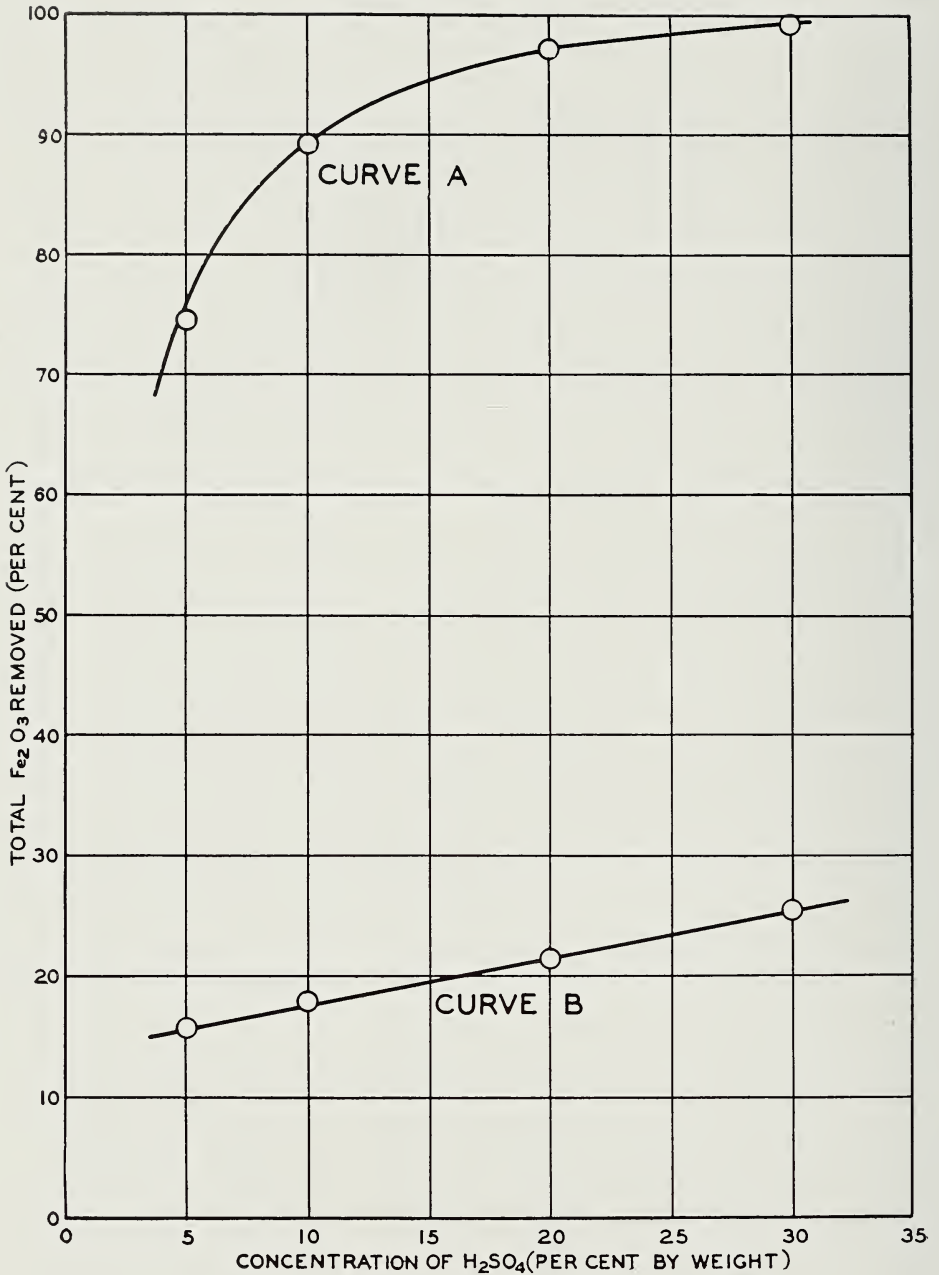


FIGURE 4

Variation in per cent of total iron present in silica which was removed by two hour treatment with sulfuric acid solutions at boiling temperature (curve A) and at room temperature (curve B).



## LEACHING WITH SULFURIC ACID

Data similar to those given above for hydrochloric acid are shown graphically for sulfuric acid in figures 4, 5, and 6. The data are recorded in tabular form in table 2. The solutions and silica were prepared and treated in the same manner as indicated above for hydrochloric acid. The time periods and the concentrations were in some cases different from those used for hydrochloric acid because it was thought, on consideration of the differences in the characteristics of the two acids, that the changes would increase the value of the data. Figures 4, 5 and 6 correspond to figures 1, 2 and 3, respectively, in the character of the data used.

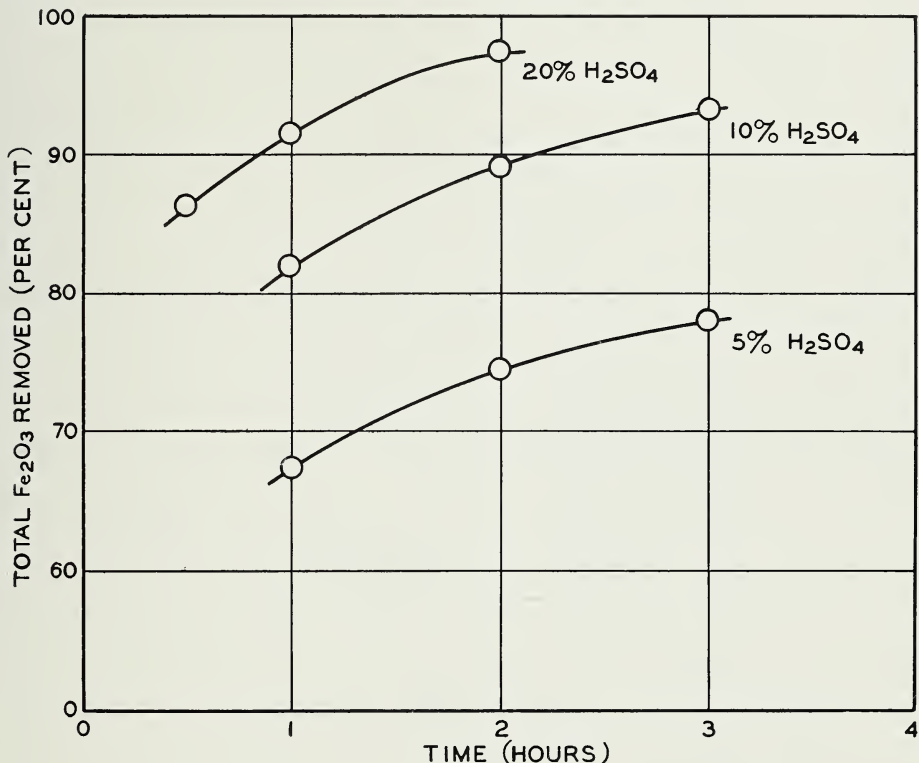


FIGURE 5

Variation in per cent of total iron present in silica which was removed by treatment, at boiling temperature for various periods of time, with sulfuric acid solutions of the indicated concentrations.

Advantages of the sulfuric acid method are: (1) Simplicity of principle; (2) High percentage of total iron may be removed; (3) Sulfuric acid is the cheapest acid we have; (4) Single reagent in the leach liquor; and (5) Reconcentration of run off and washings is much more simple than with hydrochloric acid due to the low volatility of sulfuric acid.

TABLE 2.—LEACHING WITH SULFURIC ACID SOLUTIONS

Test Number	Acid Concentration (Per cent by Weight)	Leaching Conditions	Leaching Period (Hours)	Fe <sub>2</sub> O <sub>3</sub> Removed (Per cent)
309.....	5.0	Reflux	1	67.4
285.....	5.0	do.	2	74.8
310.....	5.0	do.	3	78.4
311.....	10.0	do.	1	82.1
286.....	10.0	do.	2	89.2
312.....	10.0	do.	3	93.8
313.....	20.0	do.	0.5	86.6
314.....	20.0	do.	1	91.4
287.....	20.0	do.	2	97.2
288.....	30.0	do.	2	99.3
289.....	5.0	Room temp.	2	15.8
290.....	10.0	do.	2	17.8
291.....	20.0	do.	2	21.5
292.....	30.0	do.	2	25.2
293.....	20.0	do.	24	37.3
294.....	20.0	do.	124	59.4
295.....	20.0	do.	156	59.0
296.....	20.0	do.	175	62.9
298.....	20.0	do.	290	67.5

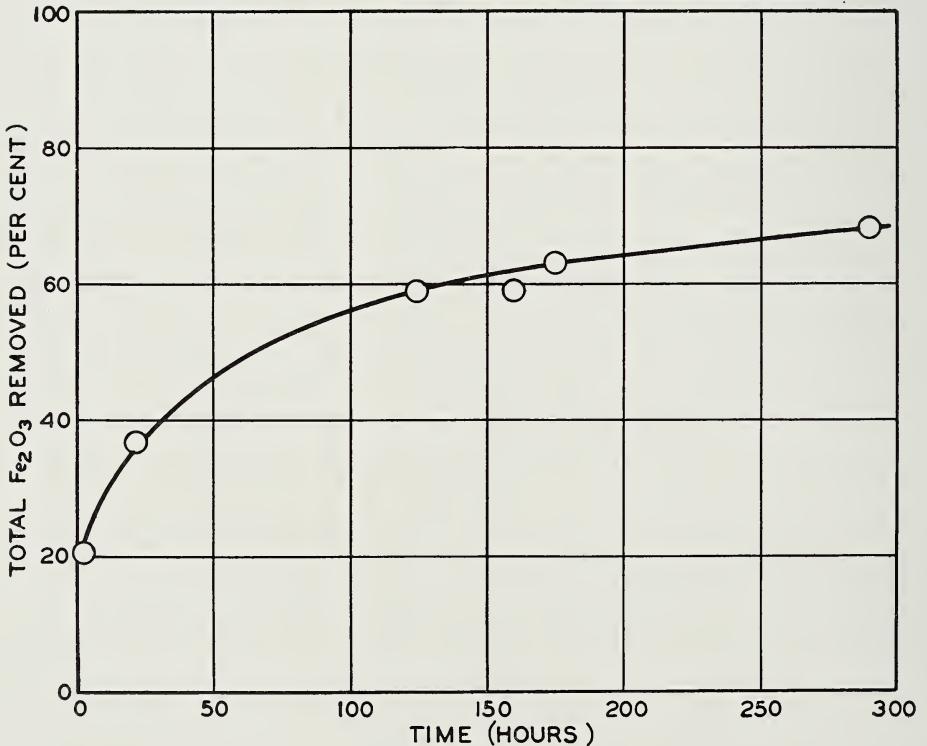


FIGURE 6

Variation in per cent of total iron present in silica which was removed by treatment at room temperature for various periods of time with sulfuric acid solution (20% by weight).

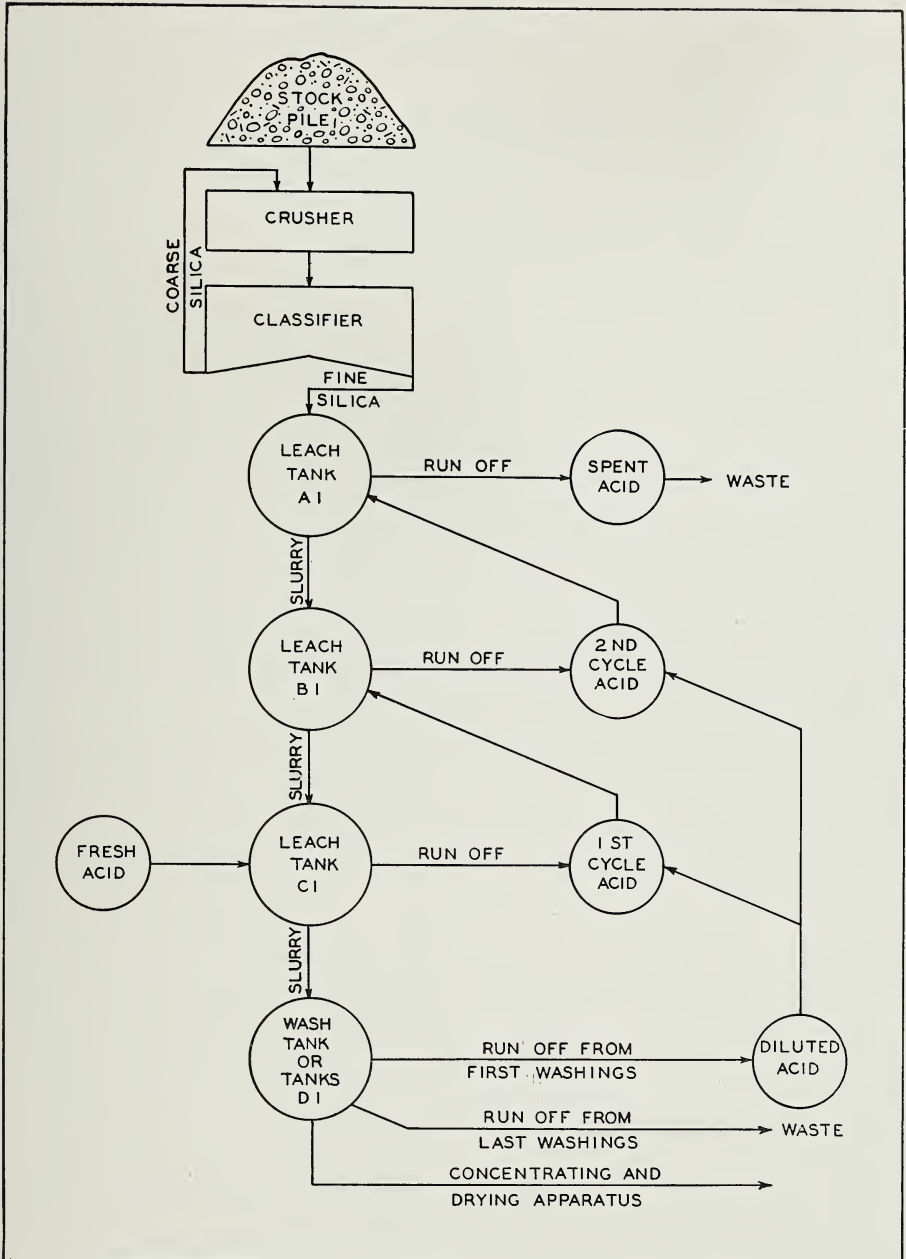


FIGURE 7

Theoretical leaching cycle using hydrochloric or sulfuric acid. Other series of tanks; A2, B2, C2, D2, etc., would be required according to the quantity of silica being treated. The tanks could be heated by direct introduction of steam.

The disadvantages are:

(1) It is necessary to work at or near boiling temperatures to get good iron removal at any concentration.

(2) It is necessary to wash out  $\text{H}_2\text{SO}_4$  very thoroughly from the product because the presence of even small amounts would tend to make the silica hygroscopic and would react with the vehicle were the silica to be subsequently used in oil paints.

(3) The liquors are corrosive. Waste might have to be neutralized by discharge on a bed of crushed limestone.

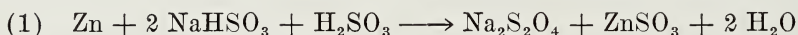
(4) The cost of  $60^\circ$  sulfuric acid at the current market (October 1937) is \$12.00 per ton. It is estimated that the cost of coal and acid for treating one ton of silica with 10 per cent  $\text{H}_2\text{SO}_4$  and reconcentrating the run off and washings to the original acid strength would be approximately \$0.50. This does not include the cost of heat to keep the batch at or near the boiling temperature during the leach because an estimate of such items, together with labor costs, interest and depreciation on capital invested in equipment, and similar items, may not be safely made before an operating cycle is developed. The items included and the assumptions made are the same as for estimating the cost of leaching with hydrochloric acid and reconcentrating. The 800 pounds of 10 per cent  $\text{H}_2\text{SO}_4$  solution which is assumed to be retained by one ton of minus  $\frac{1}{4}$ -inch silica would be equivalent to 103 pounds of commercial sulfuric acid ( $60^\circ$  Bé.) costing \$0.62.

A hot leaching process employing the counter current principle is suggested as the most promising method of applying either a hydrochloric acid or a sulfuric acid leach. Figure 7 suggests a theoretical flow sheet for such a process. Such a system is flexible enough to allow adjustment to fit variations in the type of material being treated.

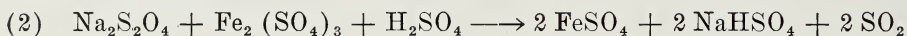
#### METAL-BISULFITE-ACID PROCESS

*Principles of operation.*—The action of the metal (zinc or iron) on sodium bisulfite forms a powerful reducing agent, presumably hydrosulfite ion  $\text{S}_2\text{O}_4^{=}$  which, in the presence of a suitable concentration of acid, converts the iron present in the silica into soluble ferrous salts which may be washed out.

The following equation is given by Roscoe and Schorlemmer<sup>39</sup> for the action of zinc on sodium bisulfite in solutions containing sulfuric acid.



C. F. Mohr<sup>40</sup> found that ferric salts are immediately reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  to ferrous salts and represented the reaction:



Two methods for applying the process suggest themselves:

1. The metal and the leach liquor together are placed in direct contact with the silica.

2. The metal is first allowed to react with the leach liquor which is subsequently applied to the silica.

To the first method the obvious objection is the necessity for separating unused metal from the bleached silica.

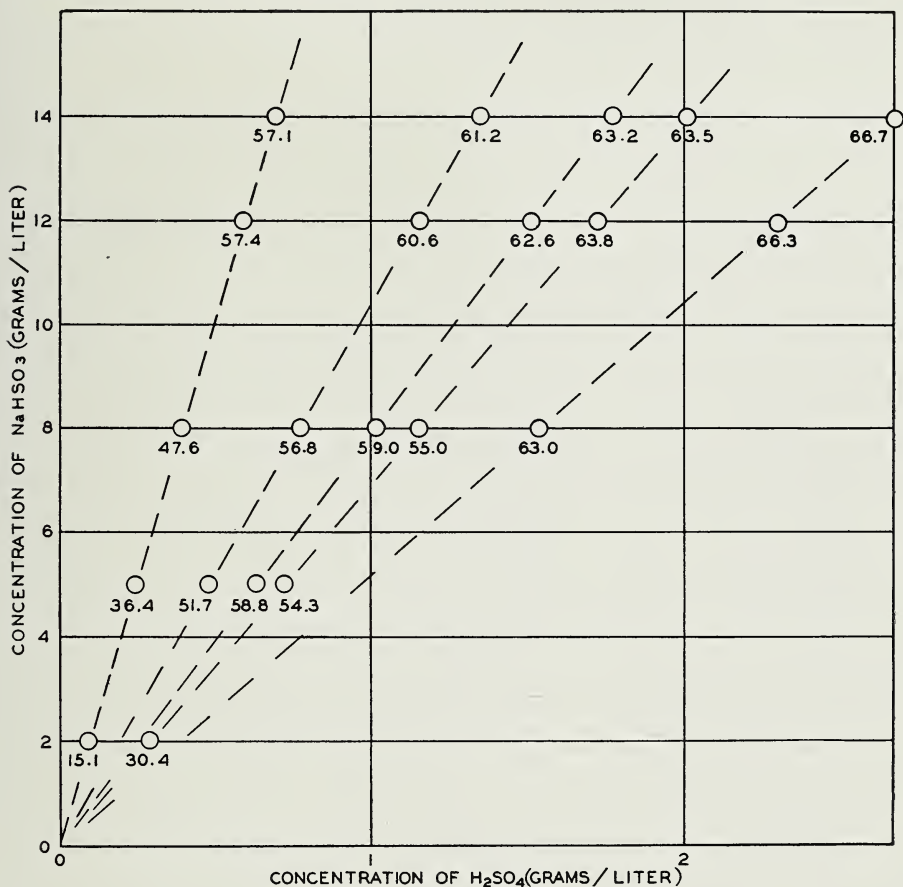


FIGURE 8

Per cent (figures below circles) of total iron present in silica which was removed by leaching the silica, in the presence of zinc, with solutions containing various mixtures of  $H_2SO_4$  and  $NaHSO_3$ .

The use of the second method results in larger consumption of chemicals. This larger consumption of chemicals is to be expected because the action of metals on bisulfites results in a variety of reduction products including hydrosulfites, thiosulfates, elemental sulfur, hydrogen sulfide and possibly other sulfur compounds in quantities which depend on conditions.

For a discussion of the mechanism of these changes the reader is referred to Mellor<sup>41</sup> who also gives a good bibliography of the original literature on the subject. It will suffice for present purposes to say that the hydrosulfite, on which we depend for bleaching silica, is very unstable in acid solution. To get the maximum effect it is therefore necessary to cause the hydrosulfite to act on the stained mineral as soon as possible after it is formed. This can be best accomplished by bringing about production of the hydrosulfite in the presence of the mineral.

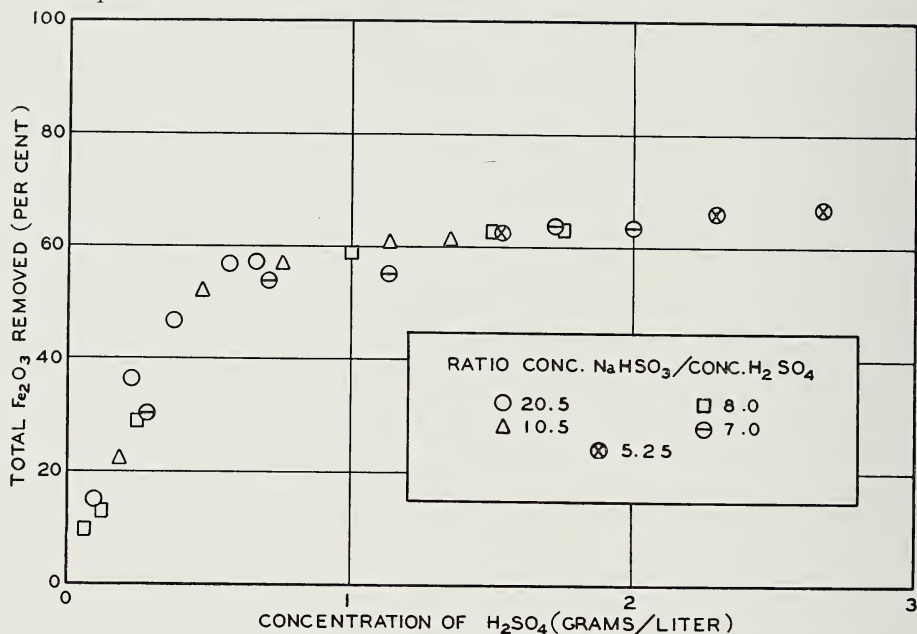


FIGURE 9

Acid concentration vs. per cent of total Fe<sub>2</sub>O<sub>3</sub> removed when different ratios NaHSO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> are employed. The same data are used in figure 8.

*Experiments.*—In our experiments either dust or 20-mesh granular zinc was used mostly as the active metal. Preliminary experiments indicated that under similar conditions iron is as effective as zinc or nearly so except that the time required to effect bleaching of the silica is possibly somewhat longer. Zinc was chosen because it was thus made possible to determine the iron removed by titration of the iron in the combined filtrate and washings from the treated silica sample. This requires only a fraction of the time that would be necessary to analyze the treated sample for residual iron.

Concentrations are expressed in terms of grams per liter throughout the following data. For those who prefer to think in the English system of units it may be pointed out that “grams per liter of solution” may be read “pounds per thousand pounds of solution” without making any important difference insofar as the solutions considered in this paper are concerned.

The results of a series of experiments relating the concentrations of acid and of sodium bisulfite to the percentage of total iron removed are shown graphically in figures 8 and 9. The same data (table 3) were used for both of the diagrams. The figures in the column of table 3 which is headed "Ratio" are not the exact values of the concentration ratios but are the approximate slopes of the broken lines on figure 8. In each experiment a 10-gram sample of silica was leached for 100 minutes in the presence of 5 grams of 20-mesh zinc. Two hundred milliliters of leach liquor were used in each test. The mixtures were shaken vigorously at 10 minute in-

TABLE 3.—RELATION OF  $H_2SO_4$  AND  $NaHSO_3$  CONCENTRATIONS TO TOTAL IRON REMOVED  
(In the presence of excess zinc)

Test Number	Concentration (Grams/liter)		Ratio $\frac{\text{Conc. } NaHSO_3}{\text{Conc. } H_2SO_4}$	Total Iron Removed (Per cent)
	$H_2SO_4$	$NaHSO_3$		
61.....	0.67	14.0	20.5	57.1
62.....	1.33	14.0	10.5	61.2
63.....	1.75	14.0	8.0	63.2
64.....	2.0	14.0	7.0	63.5
65.....	2.67	14.0	5.2	66.7
66.....	0.57	12.0	20.5	57.4
67.....	1.14	12.0	10.5	60.6
68.....	1.5	12.0	8.0	62.6
69.....	1.7	12.0	7.0	63.8
70.....	2.28	12.0	5.2	66.3
71.....	0.38	8.0	20.5	47.6
72.....	0.76	8.0	10.5	56.8
73.....	1.0	8.0	8.0	59.0
74.....	1.14	8.0	7.0	55.0
75.....	1.52	8.0	5.2	63.0
76.....	0.24	5.0	20.5	36.4
77.....	0.48	5.0	10.5	51.7
78.....	0.63	5.0	8.0	58.8
79.....	0.72	5.0	7.0	54.3
99.....	0.10	2.0	20.5	15.1
81.....	0.19	2.0	10.5	22.4
82.....	0.25	2.0	8.0	28.7
83.....	0.29	2.0	7.0	30.4
84.....	0.13	1.0	8.0	12.9
85.....	0.06	0.5	8.0	10.0

tervals. At the end of the treatment the samples were filtered, washed first with water, then with 2 per cent  $H_2SO_4$ . If good leaching efficiency was attained in the original treatment only a little iron was removed by this 2 per cent acid wash. In a characteristic instance 54.5 per cent of the total  $Fe_2O_3$  was removed by treatment followed by a water wash. On washing this same sample subsequently with 300 ml of 2 per cent  $H_2SO_4$  the per cent of the total  $Fe_2O_3$  removed was increased to 56.4. It is possible, however, that irregularities in the data such as tests numbers

74 and 79 are attributable in part to differences in the rates at which this acid wash passed through the filter.

There were two reasons for using the acid wash. First, it was known that hydrogen sulfide is among the products formed when zinc is acted upon by sulfites in the presence of acid. If the acid concentration became low enough during washing it was feared that some ferrous sulfide might be precipitated. Second, there was some possibility that basic salts of iron might be precipitated during the washing.

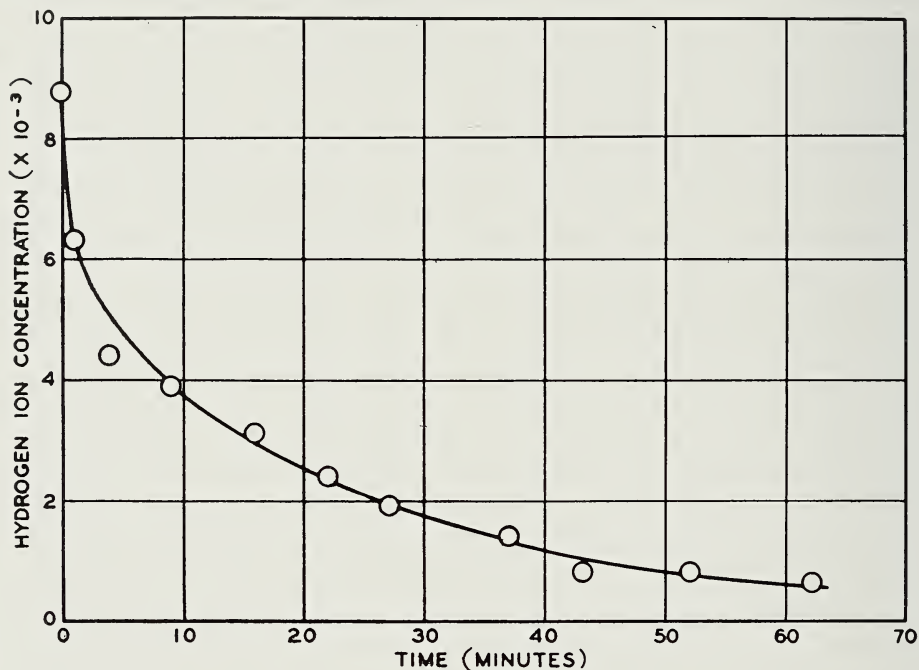


FIGURE 10

Variation of hydrogen ion concentration with time when silica is leached, in the presence of zinc, with a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{NaHSO}_3$ .

On figure 8 the figures represent the percentages of the total iron present which was removed by treatment with leach liquors of constitutions represented by the location of the circles on the diagram. It will be noted that for a given acid concentration, increase in sodium bisulfite concentration makes little difference in the amount of iron removed. Other experiments (for which data are not shown) in which the concentration of  $\text{NaHSO}_3$  was varied from one gram per liter to twelve grams per liter while the concentration of  $\text{H}_2\text{SO}_4$  was kept constant showed, within the limit of precision of the experiments, the same iron removal for all concentrations of  $\text{NaHSO}_3$  tried.



Figure 9 relates the concentration of sulfuric acid to the per cent of total iron removed using varying ratios of sodium bisulfite to the acid.

The important generalization to be drawn from these experiments is that increase of sulfuric acid concentration beyond the range one to one and one-half grams per liter causes only small increases in the leaching efficiency of these solutions.

In these experiments the ratio of leach liquor to silica was purposely kept high. It is not safe to apply the above conclusions to batches where the ratio of liquor to silica is much lower and where consequently it may be expected that the quantities of acid and of bisulfite will be largely depleted by the reactions. This is particularly true concerning the acid.

Figure 10 and table 4 show the drop in hydrogen ion concentration during the progress of an experiment in which a 50-gram sample of silica was treated with 200 ml of a leach liquor containing  $H_2SO_4$  and  $NaHSO_3$  in concentrations 1.5 grams and 8 grams per liter respectively. The data were obtained by following the pH directly with a glass electrode apparatus. They indicate a rapid consumption of acid during the early period of the leach. This corresponds roughly to the period during which iron is extracted most rapidly.

TABLE 4.—HYDROGEN ION CONCENTRATION DURING A LEACH

pH	Hydrogen ion Concentration	Elapsed Time (Minutes)
2.05	0.0089	0
2.20	0.0063	1
2.35	0.0045	4
2.40	0.0040	9
2.52	0.0030	16
2.65	0.0022	22
2.72	0.0019	27
2.85	0.0014	37
3.10	0.0008	43
3.10	0.0008	52
3.20	0.0006	62
3.40	0.0004	92
3.62	0.0002	102

Table 5 shows the falling off in the efficiency of leach liquors with increase of the quantity of silica. These tests were made with 200 ml portions of leach liquor containing at the start of the experiment  $H_2SO_4$  and  $NaHSO_3$  in the concentrations 1.5 grams and 8 grams per liter respectively. The liquor was allowed to react with a 10-gram sample of silica for 100 minutes, following which a second portion of silica was added and the leach continued for an additional 100 minute period. For the purpose of comparison with data given below it would be preferable had the silica all been

added at once and the leach stopped at the end of the first period. However, it is improbable that had this been done there would have been any difference except that slightly less iron would have been removed in each case (of the order of 1 to 3 per cent). The data of the table are shown graphically on figure 11.

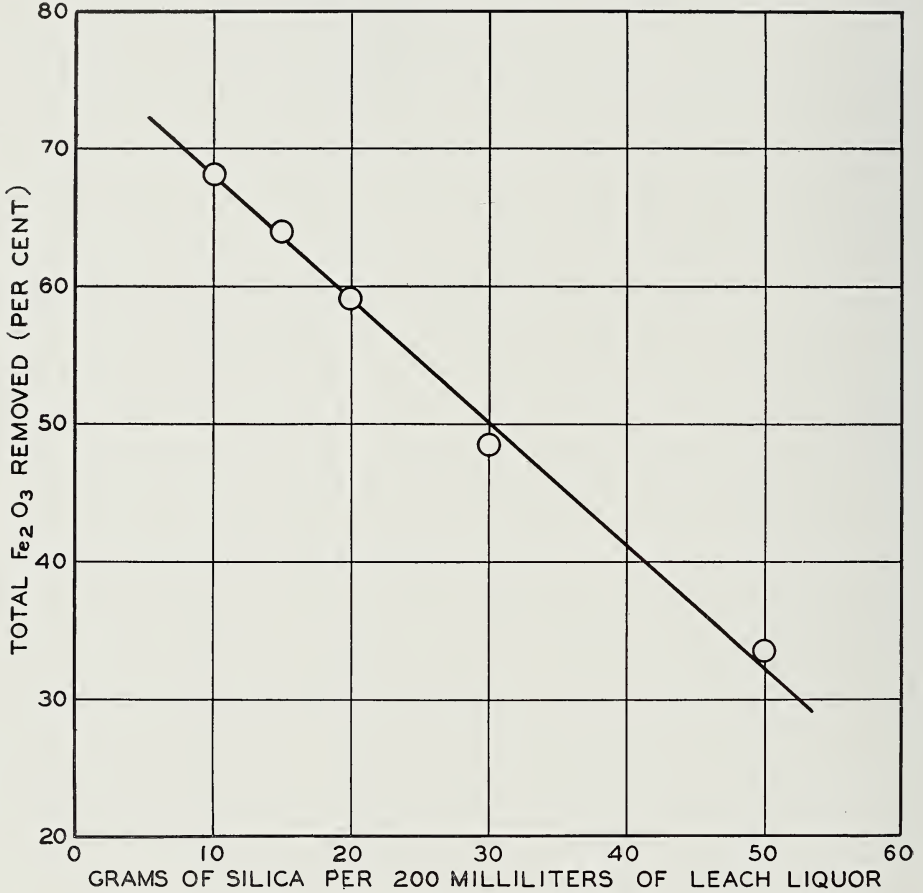
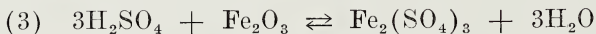


FIGURE 11

Decline in efficiency of leach liquors with increasing quantities of silica.

If it be assumed that the primary reaction is



and that other reactions affect the leach mainly by reducing the  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{FeSO}_4$  according to equation (2), page 20, it is logical to expect that the whole process will slow up as the concentration of  $\text{H}_2\text{SO}_4$  falls off. If these assumptions are approximately in accord with the facts, at least four moles

TABLE 5.—DECLINE IN EFFICIENCY OF LEACH LIQUOR

(With Increasing Quantities of Silica When No Acid is Added After the Leach is Started)

Test Number	Original Silica Sample NF212 (Grams)	Added Silica Sample NF212 (Grams)	Total Silica Sample (Grams)	Iron (Fe <sub>2</sub> O <sub>3</sub> ) Removed (Grams)	Total Iron Removed (Per cent)
108.....	10	0.0	10	0.0366	67.9
109.....	10	5.0	15	0.0518	64.1
110.....	10	10.0	20	0.0638	59.2
111.....	10	20.0	30	0.0782	48.4
112.....	10	40.0	50	0.0905	33.6
116.....	10	40.0	50	0.0922	34.2

of H<sub>2</sub>SO<sub>4</sub> should be consumed for each mole of NaHSO<sub>3</sub> consumed. For reasons to be presented later it is not practical to use a higher concentration of acid at the beginning of the leach. The other alternative is to add acid during the progress of the leach. With this idea in mind experiment No. 136 was carried out. In this experiment the pH was followed with a glass electrode pH meter. Sulfuric acid solution was added at intervals to bring the value of the pH back to 1.9. This value 1.9 is approximately the pH of the starting solution used in test No. 136. This solution contained H<sub>2</sub>SO<sub>4</sub> and

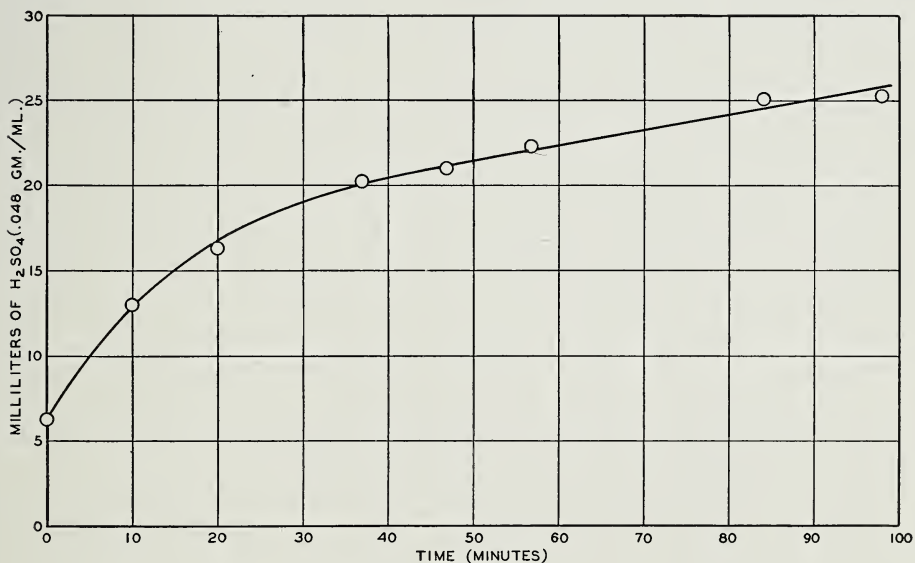


FIGURE 12

Cumulative acid additions necessary to maintain pH at 1.9 during progress of test No. 136; 50 grams silica (100 mesh, NF212), 200 ml of solution of initial composition H<sub>2</sub>SO<sub>4</sub> 1.5 grams/liter, NaHSO<sub>3</sub> 8 grams/liter, 5 grams zinc (20 mesh), added acid contained 48 grams/liter of H<sub>2</sub>SO<sub>4</sub>.

$\text{NaHSO}_3$  in concentrations 1.5 grams per liter and 8 grams per liter respectively. Figure 12 shows the data of experiment No. 136 graphically.

One possible means of reducing to a minimum the quantity of reagents used in leaching is through use of low ratios of leach liquor to silica. For the purpose of testing the feasibility of this method of leaching tests Nos. 137 to 142 described below were carried out.

In table 6 are listed data showing the results of a series of experiments in which acid was added to the batch at ten minute intervals in quantities

TABLE 6.—LEACHING WITH LOW LEACH LIQUOR TO SILICA RATIOS (a)

Test Number	Liquor Vol. at End of Treatment (ml.)	Total $\text{H}_2\text{SO}_4$ (Grams)	Total $\text{NaHSO}_3$ (Grams)	Silica NF212 (Grams)	Iron ( $\text{Fe}_2\text{O}_3$ ) Removed (Grams)	Total Iron Removed (Per cent)
136.....	219	1.215	1.6	50	0.1777	65.9
137.....	10	0.243	0.08	10	0.0351	65.2
138.....	10	0.243	0.08	10	0.0351	65.2
139.....	10	0.243	0.08	10	0.0356	66.1
140.....	10	0.364	0.08	15	0.0491	60.7
141.....	10	0.364	0.08	15	0.0504	62.4
142.....	10	0.364	0.08	15	0.0477	59.0

(a) Acid added at intervals during the leach. The time of treatment was 100 minutes in each case. Zinc employed 0.1 gm. (a large excess) of 20-mesh size per gram of silica.

estimated to maintain the pH at roughly 1.9. In these tests (except No. 136) the amounts of  $\text{NaHSO}_3$  were chosen so that its concentration at the end of the treatment would be 8 grams per liter, less the quantity consumed in the reactions. On the basis of the data of test No. 136 the estimations of the acid additions for tests Nos. 137 to 142 were made. The quantity of acid used in each of the tests of table 6 amounted to a total of 0.0243 grams of  $\text{H}_2\text{SO}_4$  per gram of silica. This acid was added in the form of comparatively dilute solutions at rates based on figure 12. The low ratio of leach liquor to silica made it impractical to follow the pH of these solutions directly because of the difficulty of quick efficient mixing of the acid in the pasty suspensions.

Test No. 136 which contained a relatively high ratio of liquor to silica is included in table 6 because it emphasizes the fact that a large excess of leach liquor is not essential to good leaching efficiency.

If all of the acid is added at the beginning of experiments, such as those of table 6, precipitation of elemental sulfur and evolution of hydrogen sulfide takes place almost immediately on addition of the zinc. If a speculation may be allowed the appearance of free sulfur probably means that the hydrosulfurous acid, on which we depend for rapid bleaching, has begun to decompose. A similar phenomenon may be observed if a solution of commercial sodium hydrosulfite be acidified. Such decomposition at the best,

results in waste of chemicals and at the worst, may result in reprecipitation of the iron as ferrous sulfide if the acid concentration runs low enough before the end of the leach.

The results of a study of this situation are shown in figure 13. Equal quantities (200 ml) of solutions containing various concentrations of sulfuric acid and of  $\text{NaHSO}_3$  were placed in contact with 5 grams of 20-mesh zinc. The solutions were agitated at intervals. The time intervals which passed before turbidity due to sulfur precipitation appeared, were noted.

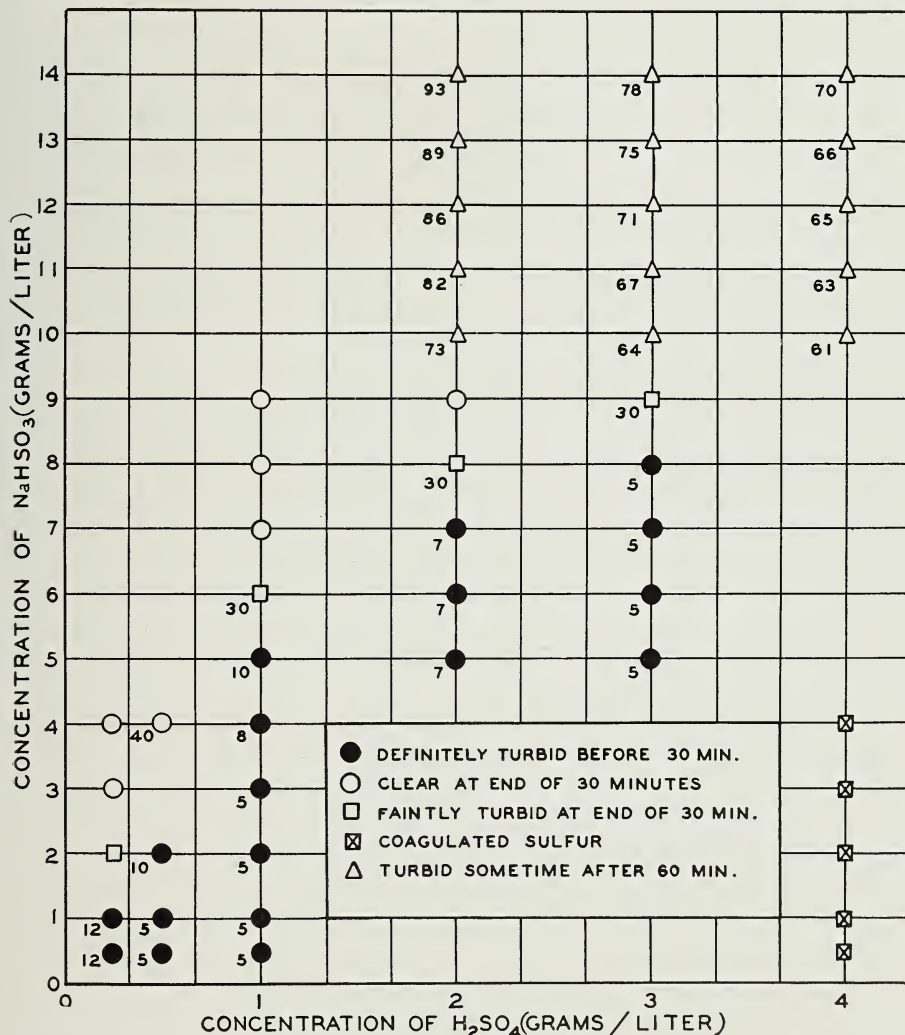


FIGURE 13

Sulfur precipitation in zinc— $\text{H}_2\text{SO}_4$ — $\text{NaHSO}_3$  water mixtures. Numbers indicate elapsed time in minutes before turbidity was detected.

If the above theory concerning the cause of sulfur precipitation is a correct one, it is to be expected that sulfur would not appear so quickly if a substance capable of being reduced by hydrosulfite ion were present. To be more explicit if iron stained silica were present the hydrosulfite would be consumed according to equation (2) almost as fast as formed as long as any easily accessible iron oxide were present.

#### APPLICATION OF METAL-BISULFITE-ACID PROCESS

Figure 14 is a suggested theoretical flow sheet for applying the process under consideration in a pilot plant. A rotating cylindrical leaching tank or at least some sort of tank with provision made for moving the metal and the silica as well as for agitating the liquor is necessary because quick bleaching takes place only on the metal surface if the metal and silica are not kept moving.

While  $\text{NaHSO}_3$  was used as a source of sulfite ion in the laboratory experiments for reasons of convenience, it is possible that in pilot plant experiments it would be preferable to use sulphur dioxide from burning sulfur or pyrite or from some other source.

Advantages of the method are:

- (1) The process works at ordinary temperatures.
- (2) The low acid concentration (of the order 0.1 to 0.2 per cent) minimizes the corrosion problem.
- (3) The quantity of acid and of bisulfite left in the treated silica after draining off excess liquor is small enough to let go to waste without excessive loss from this source. It should, however, be possible to utilize most of this by returning the first washings to the leach tank.
- (4) The action of the leach liquor is rapid in the range of effective concentrations.

The disadvantages are:

- (1) The effectiveness of the process depends on the relative amounts of three different substances—acid, bisulfite, and metal—which are added to the batch.
- (2) The acid concentration must be kept in rather narrow limits because of the instability of hydrosulfurous acid.
- (3) The fact that one of the reagents is a solid makes necessary the maintenance of a state of agitation in the batch through the period of leaching. Effective bleaching takes place only in the region close to the surface of the metal particles when there is no agitation.
- (4) It is necessary to make provision for removal of unused metal or to avoid adding metal in such quantity or in pieces of such size that complete consumption does not take place. If pieces of zinc were used some method of separation based on the difference in density of the silica and the metal

would be indicated. If iron were used a magnetic method of separation might be preferable.

(5) The method does not remove as large a fraction of the total iron as could be desired or as may be removed with acids. Sixty to seventy-five per cent of the iron present in silica samples containing 0.5 per cent to 2.5 per cent of iron reported as  $\text{Fe}_2\text{O}_3$  may be removed in a one cycle leach. No quantitative measurements were made on samples with lower iron content. We have, however, two samples of milled silica one of which was used as the mill standard of whiteness, the other was considered to be stained so badly as to be unfit for shipment on a customer's order. Our analyses showed the two samples to contain 0.04 and 0.05 per cent iron as  $\text{Fe}_2\text{O}_3$ . After treatment the stained sample was definitely whiter than that used as the mill standard.

(6) Similar processes have been the subject of a number of patents.<sup>17, 23, 24, 25, 42, 43, 44, 45</sup> It might be necessary to purchase an operating license if the method were used.

(7) Cost.

To estimate the cost of removing iron from silica by the method under consideration it is necessary to know the values of a number of variable factors. Working with silica samples containing around 0.5 per cent iron as  $\text{Fe}_2\text{O}_3$  we have been able to remove 60 to 65 per cent of the iron with various combinations of sulfuric acid, sodium bisulfite and zinc dust at costs for these reagents in the range \$0.90 to \$1.10 per ton of silica. More than half of this cost was for zinc dust. If the iron content of the silica were less the quantity of zinc required would be considerably less. The quantities of acid and sodium bisulfite would not be much less.

The above figures assume that the run off liquor is wasted. In plant practice this run off could be turned to account since it contains considerable quantities of sodium bisulfite and some acid. Experiments have shown that the iron salts that are contained in these liquors do not impair their leaching efficiencies even when present in quantity five times as great as would probably be picked up in any single leaching cycle.

If iron were used as the metal it would not be a large item in the cost of bleaching silica. As we have seen this is not the case where zinc is used. On the basis of equations (1) and (2) one gram atom of zinc would be consumed for each gram mole of  $\text{Fe}_2\text{O}_3$  removed. This is at the approximate rate of one pound of zinc per 2.45 pounds of  $\text{Fe}_2\text{O}_3$  removed. The zinc consumption under the conditions of an experimental leach is difficult to determine accurately. Our experience indicates that one pound of zinc per one and one-half pounds of  $\text{Fe}_2\text{O}_3$  removed is nearer the actual figure. The ratio will undoubtedly vary with the conditions under which the leach is carried out. Its determination is a pilot plant problem.

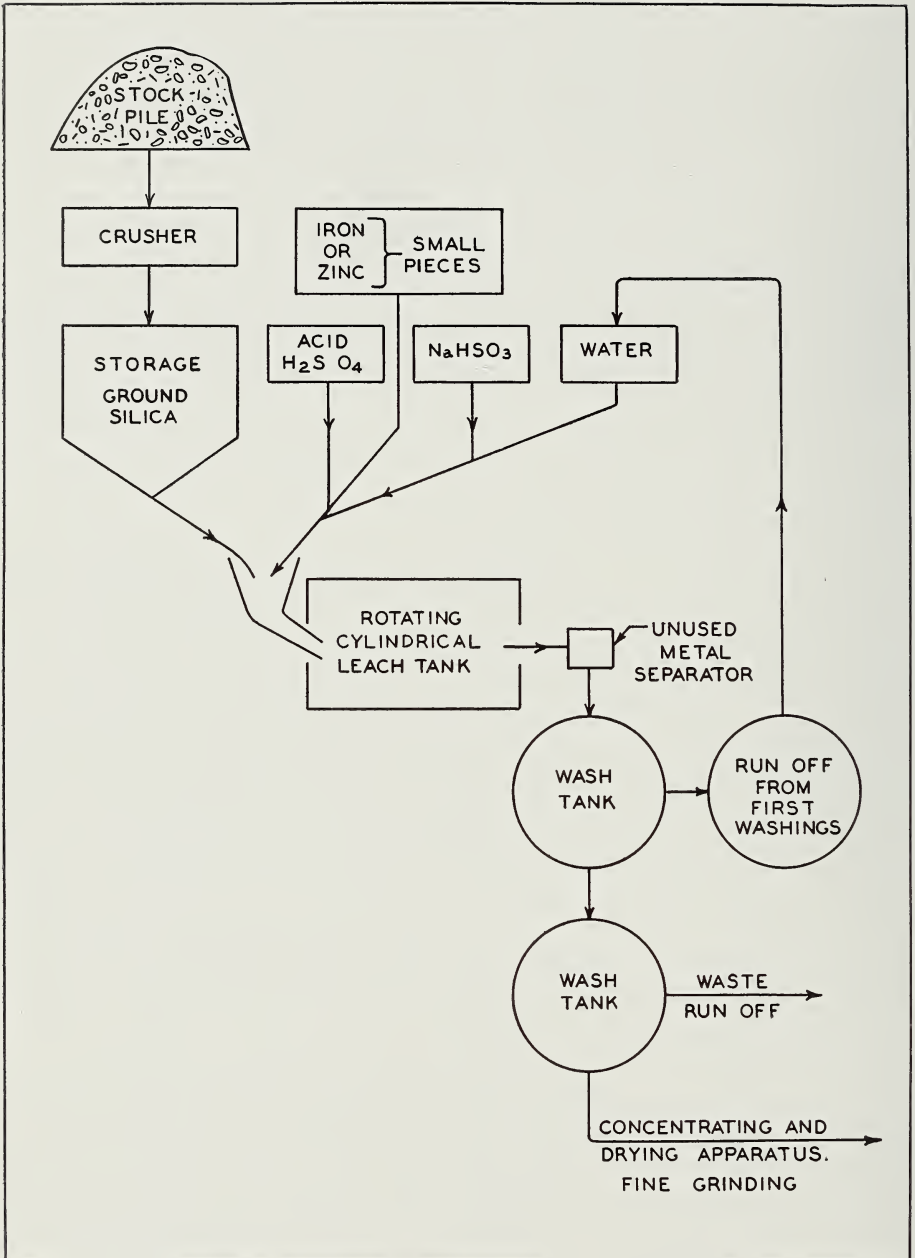


FIGURE 14

Theoretical leaching cycle employing the metal-bisulfite-acid process.



## RECAPITULATION AND REMARKS

It is technically feasible to bleach iron stained silica by any of the three processes investigated.

The efficiency of iron removal in the cases of the two acid processes varies with the temperature and with the concentration of acid and with the time. It is possible to remove by these processes well above ninety per cent of the iron present in southern Illinois silica. Advantages and disadvantages are listed.

The efficiency of iron removal by the metal-bisulfite-acid process varies with the concentrations of the reagents. The concentration of sodium bisulfite seems to make little difference provided that the total quantity of  $\text{NaHSO}_3$  present is sufficient, the measure of sufficiency being mainly controlled by the total quantity of iron removed. A concentration of as low as one gram per liter gives good results with silica of 0.5 per cent iron as  $\text{Fe}_2\text{O}_3$ . The optimum concentration of sulfuric acid lies in the range 0.5 gram to 2 grams per liter. The concentration of acid must be maintained by additions during the progress of the leach to give good leaching efficiency. The ratio of acid to bisulfite must be kept low to avoid wastage of reagents. The fact that 100-minute leaches were used is not intended to imply that it would always be necessary to use such a long period. It is considered that as a fairly reliable generalization it may be said that more than 80 per cent of the iron removed during a 100-minute leach is removed during the first 20 minutes and that more than 95 per cent of the iron removed during a three-hour leach is removed during the first hour under the conditions described above. Under conditions of vigorous and continuous agitation the time may be considerably reduced. It is necessary to agitate the batch during the leach. It has not been feasible to remove more than about two thirds to three fourths of the iron present in silica by this method.

It should be kept in mind that the above described investigations were carried out on a small number of different samples. In fact most of the data given are for a single sample. While it is not anticipated that other samples from the southern Illinois district will behave in a manner widely at variance with the behavior of the samples examined, more or less variation must be expected and large variations are always within the bounds of possibility.

## BIBLIOGRAPHY

1. Minerals Yearbook, U. S. Bureau Mines, Part III, p. 880, 1936.
2. Minerals Yearbook, U. S. Bureau Mines, p. 1,286, 1937.
3. Private Information from W. F. Bradley, Assistant Chemist, Illinois State Geological Survey.
4. Hulett, George A., Process of Purifying Inorganic Materials: U. S. Patent 1,368,396. February 15, 1921.
5. Kitaigorodsky, I. I. and Lande, L. S., Reducing Iron Content of Sands: Glass, vol. 13, p. 8, 1936.
6. Ichikawa, Y., Removing iron oxide in the clay by means of chlorine gas: Jour. Chem. Ind. (Japan), vol. 25, pp. 1310-27, 1920.
7. Flinn, Roland W., Purification of Natural Deposits: U. S. Patent 2,070,161, Feb. 9, 1937.
8. I. G. Farbenind. A-G., Decolorizing ceramic materials, white pigments, etc.: French Patent 644,547, Sept. 13, 1927.
9. Japhe, D., Purifying Sand: German Patent 560,094, August 5, 1930.
10. Vereinigte Stahlwerke A-G., Process of eliminating iron from inorganic materials: British Patent 341,060, Jan. 12, 1931.
11. Chance Brothers and Co. and English, John, Improvements relating to the removal of impurities from sand and like materials: British Patent 325,386, Feb. 20, 1930.
12. Vereinigte Stahlwerke A-G., Purifying ceramic materials: British Patent 349,033, March 15, 1929.
13. Rhodin, J. G. A., Process for bleaching sand: U. S. Patent 1,173,385, February 29, 1916.
14. Knapp, Oscar, Removal of iron in sand with chlorides: Sprechsaal, vol. 66, No. 13, pp. 215-18, 1933.
15. Ormandy, W. R., Some problems in the utilization of waste sand: Chem. Age, vol. 28, p. 111, 1933.
16. Betts, A. G., Ceramic and refractory making processes and material: U. S. Patents 1,585,826 and 1,585,827, May 25, 1926.
17. Worsley, A., Improvements in and relating to the production of hyposulphurous acid and the use thereof: British Patent 218,347, February 1923.
18. Gruber, H. and Schulze, F., Process of purifying clay, etc.: U. S. Patent 1,036,831, August 27, 1912.
19. The Exploration Co. Ltd., Decolorizing porcelain: German Patent 240,104, December 14, 1909.
20. Langford, F., Process for producing aluminum ores: U. S. Patent 1,249,125, Dec. 14, 1917.
21. Schulz, F. and Gruber, H., Removing iron from aluminum silicates, kaolin, clay, etc.: British Patent 2,309, January 28, 1914.
22. Simonson, W. W., Art of refining kaolin and similar clays for use in making pottery and like products: U. S. Patent 1,185,254, May 30, 1916.
23. Gaudin, R. F. B. and Dartmoor China Co. Ltd., Bleaching kaolin, etc.: British Patent 218,747, April 12, 1923.
24. Stubbs, A. J., A process for bleaching earthy minerals that in native deposits are stained by coloring matters that render them useless for industrial purposes: British Patent 181,132, June 12, 1922.
25. Feldenheimer, W., Treatment of earthy materials: U. S. Patent 1,573,385, February 16, 1926.
26. Societe des produits chimiques, "Alterra," S. A., Process for the elimination of iron from quartz sand, clay and other ferruginous minerals: French Patent 705,281, Nov. 8, 1930.
27. Holden, L. A., Purifying china clay: British Patent 214,699, January 19, 1923.
28. Parentani, F., Purifying clay and similar materials: British Patent 255,300, December 2, 1925.
29. Chadwick, W. T. J. and Kynaston, J. H., Innovations in the process of producing iron free alums and sulphate of alumina: German Patent 11,137, October 10, 1879.
30. The Exploration Co., Removing the coloring impurities from porcelain earth: German Patent 240,103, Dec. 14, 1909.

31. The Rockware Glass Syndicate and Adams, F. W., Improvements in or relating to the purification of silica sands and the like: British Patent 423,053, January 24, 1935.
32. Feldenheimer, W., Bleaching clay: U. S. Patent 1,588,956, June 15, 1926.
33. Kollmann, J., Purifying clays: *Glasind.*, vol. 24, no. 22, 1913.
34. Ormandy, W. R., Electrical process for the purification of clays: *Trans. Eng. Ceramic Soc.*, vol. 12, pp. 36-64; vol. 13, pp. 35-48; *British Clayworker*, vol. 22, pp. 9-18; *Ceramique*, vol. 16, pp. 142-5; *Chem. Trade Jour.*, vol. 51, p. 512.
35. Hopkins, A. I., The 'Osmotic' process for purification of clay: *British Clayworker*, vol. 22, pp. 62-3.
36. Bleininger, A. V., Use of sodium salts in the purification of clays and the casting process: U. S. Bur. Standards Tech. Paper 51, 1915.
37. Ferris, J. J., Magnetic separation in the ceramic industry: *Ceramic Ind.*, vol. 28, p. 548, 1937.
38. Feldenheimer, W. and Gee, W. J., Treating clay: British Patent 894, Jan. 19, 1915.
39. Roscoe, H. E. and Schorlemmer, C., A treatise on chemistry: The Macmillan Co., vol. I, Fourth Ed., p. 449, 1911.
40. Mohr, C. F., *Zeit. anal. chem.*, vol. 12, p. 138, 1873.
41. Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry: Longmans, Green and Co., vol. X, pp. 166-184, 1930.
42. Feldenheimer, W., Purifying clay: British Patent 242,358, August 7, 1924.
43. Feldenheimer, W., Treatment of earthy minerals: U. S. Patent 1,622,099, March 22, 1927.
44. Feldenheimer, W., Treating clays: French Patent 679,363, Dec. 11, 1928.
45. Binns, Frederick W., Method of bleaching mineral matter: U. S. Patent 2,020,132, Nov. 5, 1935.

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