

## ALUMINUM AND SILICOSIS

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### ABSTRACT

Experiments are described to show that aluminum behaves chemically toward silica under suitable conditions in a manner similar to that of mineral protectors described earlier in this Journal.

### INTRODUCTION

The paramount importance of silicosis to industry, classified by some authorities as the leading industrial disease today, has by its impact overcome much of the inertia once so prevalent in the general attitude toward it. An early development, and one to be credited with real success, is that of dust elimination, though it is really dust reduction only. The limitation of this procedure is the high cost, especially of removing the finest fraction, with the all too common result that this remains. Many regard this last trace of dust as the most harmful. Admixed mineral protector dusts have been suggested to render harmless this fine material, thereby requiring elimination only of the more easily and cheaply removed first fraction. This paper is concerned with these protector dusts.

In an earlier paper to which the senior writer contributed,<sup>1</sup> a mineralogic explanation of protectors was offered. Since then Denny, Robson and Irwin have discovered the protective influence of aluminum and in announcing their discovery have suggested a wholly different explanation.<sup>2</sup> We feel that it is essential to the proper use of a protector to understand the principles of its operation. To that end we are disagreeing with the *explanation* of Denny, Robson and Irwin, while accepting the conclusions of their animal experiments that *aluminum is a protector*. Our subject matter is therefore unavoidably controversial. Our purpose is to show (1) that the presence of aluminum, as a protector substance does not decrease the solubility of silica in aqueous solution, but that it removes dissolved silica from solution, (2) that this effect of aluminum on dissolved silica is not the basis of its protective capacity, (3) that the basis of the protective capacity of aluminum is its ability to flocculate colloidal silica as do other protector substances described earlier in this journal, and (4) that certain reactions of aluminum and the alkaline earth carbonates toward silica are similar.

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## THE PROBLEM

The literature on silicosis has credited the property of protection to the following: shale,<sup>3</sup> carbon, the alkaline earth carbonates,<sup>1</sup> iron oxide,<sup>1,4</sup> gypsum,<sup>4</sup> and Portland cement.<sup>5</sup> It has been suggested that the essential protective feature of these substances is their ability to flocculate silica, based on the charge which they carry in the appropriate medium, rather than to inhibit solution of silica. Aluminum is shown by an electrophoresis test to carry a charge in dilute sodium chloride solution similar to that of the protectors listed above, and we believe therefore that it acts as a protector in a manner comparable to these substances. This is an important distinction, since the effective practical use of any protector is made possible by an understanding of the principle on which it operates. If, for instance, the protection afforded by aluminum is dependent on its capacity to inhibit the solubility of silica as Denny, Robson and Irwin believe, then we are dealing with a rather specific property which would be expected to vary in effectiveness with the nature of the siliceous material. In this case it would be necessary to determine its specific protective capacity against each noxious element of industrial dusts. But if the protective influence is like that of the other protectors listed, that is, dependent on its ability to flocculate silica, then its protective capacity apparently covers all siliceous materials which hydrate or dissolve under the conditions in which we are interested and release colloidal silica. Furthermore, additional potential protectors, may be found by first making electrophoresis tests on colloidal suspensions of the materials under consideration.

Protectors, as we understand them, flocculate disperse material in body fluids, as they are known to do in laboratory solutions. This flocculation is tantamount to a reduction in the number of discrete units to be phagocytosed. † This function of protector materials is outlined in an earlier paper to which the interested reader is referred.<sup>1</sup>

The experiments of Denny, Robson and Irwin show that aluminum protects animals against silicosis. They explain this protection by stating that "the addition of small quantities of aluminum dust almost completely inhibits the solubility of siliceous material in the beaker." They define solubility as ". . . the concentration of silica in solution obtained under the conditions noted." They determine the silica in solution "colorimetrically by the method of King and Dolan." The colorimetric method of King and Dolan indicates silica in the soluble form almost exclusively as distinct from particulate or colloidal silica.<sup>6</sup> An absolutely sharp distinction is of course never possible since ordinarily colloidal

† An analogy may be drawn to opsonization.

silica is contributing to the amount of silica in solution. The analytical results of Denny, Robson and Irwin being thus concerned with dissolved silica do not take into consideration the particulate silica. But suspicion rests heavily on particulate silica as the cause of silicosis. This view is not only widely held but was convincingly expressed in 1936 by F. G. Banting,<sup>7</sup> who, after describing experiments performed in his laboratory, says, "These experiments show that when silica is in the soluble form it is readily transported in the blood stream, and, since it is rapidly excreted by the kidneys, it does not produce fibrosis." And again he says, "It would therefore appear that fibrous nodules form as a result of particulate silica and not of dissolved silica." Denny, Robson and Irwin state that "Gye and Purdy were the first to point out that the chemical reaction and not the physical presence of siliceous material was responsible for the production of the fibrosis in silicosis." Gye and Purdy used colloidal silica in their experiments, the results of which were published under the title, "The Poisonous Properties of Colloidal Silica." There is no known quantitative relationship between the dissolved silica revealed by colorimetric analysis and the particulate silica present in any one solution. It would seem inadvisable, therefore, to attempt to explain the protective influence of aluminum solely on its effect on the dissolved silica revealed by colorimetric analysis. Attention may be called to a most significant statement by Gye and Purdy pertaining to the effect of colloidal silica on rabbits. They say<sup>8</sup>—"We have come therefore to regard the dose of 5 mgm . . . as being on the borderline of poisonous doses. *This applies only to freshly prepared highly dispersed sol; in older preparations of silica sol in which aggregation has occurred much larger doses may be given without producing lesions.*" (The italics are ours.) In other words, silica in the flocculated state—the objective of a protector—lacks potency. It is possible that a part of the reduced effect of the "older preparations" is to be attributed to an increase in the proportion which is in solution and a corresponding decrease in the quantity of colloid, though the authors do not formally mention it.

#### RELATIONSHIP OF ALUMINUM TO DISSOLVED SILICA

Let us examine the "beaker experiment" of Denny, Robson and Irwin, namely, that two identical samples of silica, one with aluminum, are treated with water and filtered—the filtrate from aluminum and silica contains no silica, the other does. We suggest that the silica has been equally dissolved in both cases, but the aluminum present in the one has removed the silica from solution by adsorption or chemical combination. The silica thus tied to the aluminum does not pass through the filter paper and does not appear in the analysis of the filtrate. We shall

prove this statement experimentally and show that not merely aluminum, but similarly any one of several metallic ions (such as, magnesium, calcium, zinc, tin, iron or nickel) which, like aluminum, forms a relatively insoluble flocculent hydroxide in mildly alkaline solution is capable of removing silica from that solution.

We duplicated the "beaker experiment" of Denny, Robson and Irwin to assure ourselves that we were employing essentially the same technique. Following their procedure, we then prepared a silica solution by agitating one gram of -10 micron quartz dust in 100 cc. of distilled water at 37.2°C. for twenty hours. This solution was filtered, analyzed colorimetrically for silica,\* and then divided into two portions. To one part of the filtrate was added .1 gram of "Aluminum Bronze" powder (manufactured by Baer Bros., New York) which had been previously washed in acetone, and both parts were again agitated for twenty hours. These were filtered and analyzed colorimetrically. The analyses showed that silica had been removed from the solution containing aluminum, but had remained essentially the same in the other. The procedure was repeated with one modification—the *pH* of the solutions was kept below 5 by the addition of HCl. The silica was *not* removed since the aluminum was forming  $\text{AlCl}_3$  instead of hydrolyzing. The procedure was repeated again allowing the aluminum a few minutes only to operate instead of twenty hours. Silica was not removed from solution. It is thus apparent that aluminum has the capacity to remove silica from nearly neutral aqueous solutions, if given sufficient time to operate.

Aluminum hydrolyzes in neutral solutions and forms  $\text{Al}(\text{OH})_3$ , a highly insoluble, flocculent substance which is capable of adsorbing, or chemically combining with many dissolved substances. To test the effect of  $\text{Al}(\text{OH})_3$  on silica in solution, the following experiment was run: 50 cc. of a previously prepared silica solution of known concentration was made 0.01*N* in respect to  $\text{AlCl}_3$ . This solution was neutralized with  $\text{Na}(\text{OH})$ , shaken for one minute, and filtered free of the precipitated  $\text{Al}(\text{OH})_3$ . Colorimetric analysis of the filtrate showed complete removal of the silica. A similar solution was prepared, in which the *pH* was kept below 5 to prevent formation of  $\text{Al}(\text{OH})_3$ , filtered and colorimetrically analyzed. There was *no* reduction in silica. Therefore, freshly precipitated  $\text{Al}(\text{OH})_3$  is capable of immediately removing silica from solution. Similar tests were made with other flocculent metallic hydroxides. To prepared silica solutions of known concentrations were added soluble salts of magnesium, iron, tin, zinc, calcium and nickel, in quantity sufficient to make them 0.1*N* in respect to these metallic ions. The solutions were

\* We define "dissolved silica" as that which is revealed by colorimetric analysis. This we believe gives the same meaning to the term as that of Denny, Robson and Irwin.

then made alkaline with NaOH, filtered and analyzed colorimetrically. The major portion of the silica was removed in each case. It is evident, then, that aluminum hydroxide and these other hydroxides can remove silica from solution.

Another experiment was run to show that the presence of aluminum with silica in aqueous solution has no apparent effect on the total amount of silica which dissolves. In separate flasks, one with aluminum and one without, quartz dust was agitated with water for twenty hours, filtered and analyzed colorimetrically. As before, one filtrate contained silica and the other had almost none. The two filter papers with the residues were next treated with 100 cc. each of 1.2*N* HCl and again filtered. NaOH was added to the filtrates, since the silico-molybdic acid color used in the colorimetric test for silica is not so intense in strongly acid solution. However, in order to prevent  $\text{Al}(\text{OH})_3$  from precipitating, the *pH* was not allowed to rise above 5. The solution containing aluminum showed silica, the other showed very little. The silica found here had of course been released by dissolving the aluminum. Furthermore, the silica found here was sufficient to indicate equal solubility as indicated by colorimetric tests in both cases—one with aluminum, the other without. That is, the silica dissolved by water alone, as revealed in the filtrate, plus that resulting from the HCl treatment of the filter paper containing quartz alone is equal in amount to the trace in the filtrate from quartz and aluminum in water plus the larger amount resulting from the HCl treatment of the filter paper containing quartz and aluminum. It is evident, then, that the presence of aluminum does not apparently modify the amount of silica which dissolves.

#### RELATIONSHIP OF ALUMINUM TO PARTICULATE SILICA

Let us now examine the effect of aluminum on particulate silica and compare this effect with that of other protectors already identified.

Silica dust which has been agitated in distilled water cannot be completely filtered out to yield a clear solution by using either fine-grained paper or a thick asbestos pad in a Gooch crucible. The combined use of gravimetric and colorimetric analysis shows that the smaller portion of the silica which is present in such a solution is in the soluble form and the larger portion is in suspension. The suspended particles are in a disperse state, each with the same charge, and these will not flocculate or combine into aggregates large enough to remain on the filter medium. If a suitable substance carrying an opposite charge is added to the suspension, flocculation occurs and filtration yields a clear solution. Tests were made by adding aluminum, carbon, hematite, calcite, Portland cement and gypsum to separate portions of a cloudy filtrate of silica in water. These

solutions were shaken one minute and filtered. In each case the filtrates showed almost complete removal of the visible suspended silica. (We did not deem it necessary to make quantitative analyses.) A control without a flocculating agent was filtered a second time and showed no visible reduction. Aluminum, like these other protectors, will flocculate suspended silica.

It is generally recognized that electrolytes will bring about flocculation of disperse suspensions, some requiring greater concentration than others. This phenomenon is discussed in any text on colloid chemistry. To test the effectiveness of flocculation by neutralization of the silica charge by that carried by a strictly particulate protector, we chose carbon, since it is insoluble in water and does not furnish ions to the solution. Cabot's lamp black was deactivated by heating in the absence of air in a platinum crucible over a Meeker burner, and then repeatedly extracted with boiling distilled water.\* One gram of this carbon was agitated twenty hours at 37.1°C. with one gram of silica in 100 cc. of distilled water. A second flask with silica alone in water was run as a control. The filtrates of these flasks were analyzed colorimetrically and found each to contain 4 mg. of silica per liter of solution. Gravimetric analyses were next made and showed a reduction from 173 mg. of silica per liter of the control filtrate to 17 mg. per liter of the silica-carbon filtrate. These results emphasize the effectiveness of flocculation of particulate silica by a non-ionizing substance.

The following statement is made by Denny, Robson and Irwin—"The solubility of quartz is increased by the presence of small amounts of the carbonates—of magnesium—and calcium." This statement is true, but the obvious implication, which has already been expressed by others,<sup>9</sup> is that these carbonates increase the silicosis hazard by their presence. This is based on the apparent belief that silica in solution is the cause of silicosis. On the other hand, since these carbonates carry in body fluids a charge opposite to that carried by silica particles, they tend to flocculate the silica and may thus serve as protectors. The efficacy of magnesium carbonate may be questioned on another basis—it is so much more soluble in water than calcite that it might dissolve before its protective purpose is fulfilled. This can be answered only by animal experiments for which others are better qualified.

#### TO RECAPITULATE

In the lung the harmful influence of silica is apparently at its peak when the silica is present as a colloid. The system is unable to handle it

\* A high *pH* carbon should be used, since these are positively charged in nearly neutral solutions. All carbons are not equally satisfactory.

in this state. Our chief conclusion is that the action of a protector, whether mineral or metallic, seems to be to collect this disperse silica into unit aggregates which may be removed by phagocytosis.

Since it has been shown that aluminum does not modify the ability of silica to pass into aqueous solution, and since it has been shown that aluminum flocculates silica in suspension, aluminum is recognized as another protector of the type already described in the literature.

Still other potential protectors, more suitable than any of these for specific industrial purposes, may be selected by methods described.

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#### REFERENCES

1. Emmons, R. C., Wilcox, Ray, *Am. Mineral.*, vol. **22**, p. 256, 1937.
2. Denny, J. J., Robson, W. D., Irwin, D. A., *Can. Med. Assn. Jour.*, vol. **37**, pp. 1-11, 1937.
3. Haldane, J. S., *Trans. Inst. Min. Engr.*, vol. **55**, p. 264, 1918; *Chem. Met. and Min. Soc. South Africa*, vol. **30**, p. 54, 1929.
4. Gardner, L. U., Report of the Director for the year ending Sept. 1936, Saranac Laboratory for the Study of Tuberculosis, p. 7.
5. Briscoe, H. V. A., Matthews, J. W., Holt, P. F., and Sanderson, P. M., *Bull. Inst. Min. and Met.*, April 1937, June 1937.  
Briscoe, H. V. A., *Nature*, vol. **140**, p. 773, 1937.
6. King, E. J., and Stantial, H., *Biochem. Jour.*, vol. **27**, p. 1007, 1933.
7. Banting, F. G., *Can. Med. Assn. Jour.*, vol. **35**, p. 289, 1936.
8. Gye, W. E., Purdy, W. J., *Brit. Jour. Exp. Path.*, vol. **5**, p. 238, 1924.
9. Editorial—*Can. Med. Assn. Jour.*, vol. **37**, p. 381, 1937.