FILE NAME: ALCOA (ALC)

DATE: 1941 Apr 2

DOC#: ALC059

DOCUMENT DESCRIPTION: Letter

Aluminum Company of America

ALUMINUM RESEARCH LABORATORIES

POST OFFICE BOX 772

FRANCIS C. FRARY
DIRECTOR

New Kensington, Pa.

April 2, 1941

Dr. Leroy Gardner, Director
The Saranac Laboratory
Saranac Lake, N.Y.

Dear Dr. Gardner:

I have your letter of the 25th, and want to assure you that we will be very happy indeed to give you all the information we can, and that you need have no hesitation in writing as often and as fully as you desire, because we are vitally interested in your problem.

The question of the "solubility" of silica is one which is quite involved, and I do not pretend to know very much about it. It does seem possible, however, that silica in the form of silicates in solution might ionize differently and behave quite differently from silica in the form of the hydrated and probably colloidal silicic acid derived from extremely finely divided quartz. Thus, for instance, if you had a calcium-sodium silicate I would expect that if it went into solution it would hydrolyze to sodium ions, possibly some calcium ions and a complex anion containing both silica and some of the metals.

On the other hand, silica on going into solution would be expected to hydrate into the form of some silicic acid such as H_2SiO_3, which might partially dissociate into hydrogen ions and SiO_3 or $HSiO_3$ ions, but also would probably largely

exist in an undissociated state, because these very weak acids do not usually dissociate as strongly as their salts. Whether it is the SiO_3^{++} or $HSiO_3^{+}$ or the undissociated silicic acid which has a physiological effect is, of course, beyond our power to determine, but I can see that there might be a difference between the behavior of such solutions and those of a silicate irrespective of the total amount of total chemically determinable SiO_2 in "solution".

Also, I am wondering whether your quartz was fine enough to give you a maximum effect, since you mention that the minerals used were from 1-3 microns. We know, of course, from experience in the Laboratories that solid quartz is very little affected by water, and, as I understand it, you and others have proved that it is only the fraction below 3 microns which is of physiological significance. Obviously, then, the particles which are finer than 1 micron, because of their large surface in proportion to their weight, are most easily attacked by the water, and consequently the "solubility" obtainable with a given sample of quartz will depend considerably, I would suspect, on the amount of these extremely fine particles present. Also, of course, some samples of quartz contain a little alkali, and I assume that would make a difference in the solubility. However, the whole question of the mechanism of the action of quartz is certainly worthy of much further study.

Dr. Irwin was down here yesterday to talk before the Western Pennsylvania Association of Safety Engineers, and I asked

him about the technique employed in getting the effects which he shows in his paper, by the injection of mixtures of quartz and aluminum into animals. He said that they had had quite a little trouble at first in not being able to get the aluminum powder well dispersed with the quartz. I suspect this is because the powder, even after washing with acetone, still contains a considerable amount of grease adsorbed on its surface. Consequently, it tends to clump together. After some preliminary difficulties, in which microscopic determination showed that his aluminum had not been well dispersed with the quartz, he developed a special technique, and I have asked him to write me a detailed description of it for your information. I will send it along as soon as I get it.

I know that Dr. Blaisdell was worried about the possibility that the heat employed in sterilization might destroy the protective action of the powder, but I think this is due to a misapprehension on his part. The powder which they produce in their grinding experiments has no grease upon it, but it has been oxidized to the extent of about 50% in the course of its preparation. When placed in water at body temperature over night, substantially all of the aluminum reacts with the water, and when he used 0.1% of the powder (containing only 50% of aluminum) and 5cc of water he got a considerable amount of gelatinous material in the water, but, as I recall it, the solution did not solidify. When he used the same amount of our powder which had been heated, which probably contained upwards of 90% metallic aluminum, he found it a little slower to react, but when the reaction was

complete the solution had taken the form of a stiff jelly full of gas bubbles. To me that simply means that because he had nearly twice as much aluminum in the sample used, he got twice as much aluminum hydroxide, and consequently a stiffer mixture with the water. I very much doubt whether there is any injurious effect due to the heating. Actually, the effect of heating seems to be to oxidize and destroy the remnant of grease, and make the aluminum reactive so that it will, in the first place, be thoroughly wet by water and, in the second place, be more or less completely attacked and oxidized by the water in the course of about 24-36 hours. The amount of actual oxidation of the powder during the heating (if the powder does not catch fire, which it sometimes does when we have tried to heat larger quantities) is probably only a few per cent, and the amount of metallic aluminum left would be considerably greater than that in the dust produced by grinding. Since obviously the effect of the aluminum dust in the lungs is to produce soluble or colloidal aluminum hydroxide, it is evident that it should have a similar effect to that which you have found with your aluminum hydroxide, and I think that if you get a chance to repeat your experiments with the technique that Dr. Irwin employed, you will probably find the same results that he did.

I was much interested in the sample of precipitated "aluminum hydroxide". I had an analysis made of it and, as I suspected from your method of preparation, we found that it contained 3.40% of chlorine. It also contained 7.82% of water lost

below 110°C, which we consider to be adsorbed moisture, and 25.31% more of water which we call "loss on ignition", and which is the amount of water given off (based on the weight of the dried sample) when the sample which has been dried at 110° is heated to the highest temperature of the blast lamp. You will note that this amount of water is intermediate between the amount required for the so-called trihydrate ($Al(OH)_3$) and the monohydrate (AlO.OH). The very fine C-730 hydrate, of which I sent you a sample, is the alpha trihydrate ($Al(OH)_3$). One would think that your sample was probably a mixture of a basic chloride with more or less monohydrate and trihydrate. We had an X-ray pattern made of it in order to try and identify it, and the report is as follows:

> "The X-ray diffraction pattern of the alumina hydrate revealed only a trace of an extremely fine grained alpha monohydrate. The absence of any weak, medium and intense diffraction lines on the photogram would suggest that the hydrate consists chiefly of amorphous material or that the grain size is extremely small."

We know that the presence of the chlorine in the material precipitated in this fashion very materially assists in peptizing the aluminum hydroxide, and it apparently also prevents the formation of any appreciable amount of crystalline particles of a size large enough to give a diffraction pattern. We also had a particle size determination made, and the laboratory reported that most of the particles were about 10 microns in diameter. Of course this would be pretty coarse for a dusting experiment. We would have no means of producing a quantity of this hydrate by any way except to repeat in the laboratory the

NK 1616 5M-7-38 PRINTED IN U.S.A.

same method of preparation which you have employed. Our C-730 hydrate is, however, so much finer (average particle size about 0.5 micron) that I would expect it would function about as well in inhibiting the action of silica as the more easily dispersible material you have made, even though it is probably more slowly attacked per unit of surface area because of its crystalline character. The activated material will probably be definitely more reactive than the regular 730.

I believe that Dr. Robson at one time made some experiments in which he attempted to dust animals with some hydrated alumina which we supplied him, but which was not as fine as our C-730 grade. He had some trouble with pneumonia and lung abscesses in these animals, and apparently did not get any results which were conclusive. I think that the finer material such as the C-730 would probably not produce any physical irritation.

I am sorry that I did not get an opportunity to go to the Ceramic Society meeting, but that is one of the societies whose work does not touch ours very closely, so that I do not attend their meetings. I shall hope, however, to see you at some other meeting, and in the meantime will be very glad to have your further comments on this situation, and to give you any further information that I can in connection with your experiments. We are all very much interested in this peculiar effect of aluminum hydroxide, and anxious to be of any assistance we can.

Very truly yours,

FCF:ML

Director
Aluminum Research Laboratories