Aging of Reagent Solutions in Precipitation Processes

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Introduction

The effect of the length of time during which a solution of barium chloride is allowed to age, prior to its use, upon the particle size of precipitated barium sulfate has been investigated by Bogan (1), (2) and by Fischer and Rhinehammer (3). Both found that barium sulfate crystals precipitated from a fresh solution of barium chloride are smaller than those from an aged solution. Bogan also found that filtered, fresh barium chloride solutions produced larger barium sulfate particles than did unfiltered, fresh solutions. Fresh solutions prepared from finely ground barium chloride resulted in small particles, while a solution prepared from one large barium chloride crystal gave larger particles. Bogan concluded that a fresh barium chloride solution had undissolved barium chloride particles present which acted as additional nuclei. Presumably filtration would remove these particles by adsorption, and aging by a combination of adsorption and dissolution.

Rhinehammer investigated the effects of the previous history of the water used to prepare the solution and the container in which the solution was aged. All combinations resulted in larger particles with an aged solution than with a fresh solution, but the magnitude of the effect varied widely. It was noted that precipitates prepared from still older solutions consisted again of small particles; this observation is not compatible with Bogan's theory. Benedetti-Pichler (4) ascribed the aging effect to impurities in the barium chloride which are adsorbed on the container on aging. He found that a fresh solution of recrystallized barium chloride produced large particles, but other workers have observed the aging phenomenon even with highly purified barium chloride. This explanation also fails to explain the production of small particles from still older solutions.

The purpose of the present study was to investigate further this aging phenomenon using a variety of experimental methods. An attempt was made to obtain further experimental data, either to support or to reject previously proposed explanations. An attempt was also made to ascertain whether or not a similar phenomenon occurs with other solutions and in other precipitation processes.

Experimental

1. Effect of Filtration

Precipitations of barium sulfate were made with both fresh and aged solutions of barium chloride and also with solutions which had been filtered when fresh and then aged. The barium chloride solution

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was 0.02 molar. The sodium sulfate solution was 0.016 molar, with the pH adjusted to 1.0 with hydrochloric acid. The mixing of equal volumes of solutions resulted in a twenty-five percent excess of barium ion. Average particle sizes of barium sulfate were determined by measurement with a light microscope equipped with a micrometer eyepiece.

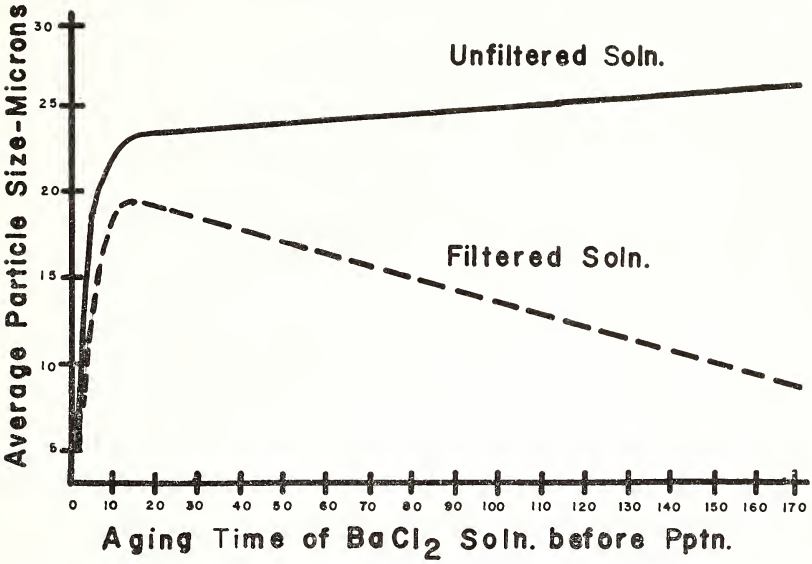

Figure 1.

Typical results are shown in figure 1. The solid line represents data for a barium chloride solution which was aged without filtration. The broken line represents data obtained with a barium chloride solution which was filtered when fresh and then aged. A projection of the solid line to an aging time of one month indicates a decrease in size to seven microns. Barium chloride solutions which had aged for long periods of time produced two sizes of particles. This could be due to particles forming both by spontaneous nucleation and from nuclei of impurities, perhaps dissolved from the walls of the container.

The effect of filtration appears to be one of speeding up the complete cycle of the aging process rather than one of eliminating the phenomenon. The data of figure 1 are for filtration through a sintered porcelain crucible; filtration through filter paper and a Seitz bacteriological filter produced similar results.

In other experiments a Bausch and Lomb Spectronic 20 spectrophotometer was used to measure optical density of suspensions of the precipitate in its mother liquid. The optical density should be a direct function of the total surface area of the precipitated particles, and this in turn should be an inverse function of average particle size. This procedure should give a more representative measure of average

particle size than the direct microscopic measurement. The two methods did, however, compare favorably with each other.

2. Effect of Mixed Solutions

It was thought that perhaps nuclei present in a barium chloride solution would result in the formation of large particles of barium sulfate rather than small ones. That is, the barium sulfate crystals would form around these "seeds," and particles resulting from spontaneous nucleation would be negligible. If this were the case then an aged barium chloride solution, which results in large barium sulfate particles, should contain more nuclei than a fresh solution. To test this supposition mixtures of half fresh and half aged barium chloride solutions were used to precipitate barium sulfate. Average particle sizes were determined both by microscopic and by spectrophotometric measurement. All particles formed were of small, uniform size, no matter how old the aged half of the barium chloride solution. This result indicates that the fresh half of the solution controls the size of the particles. Since these are all small, the fresh solution must contain the additional nuclei which cause the small particles. Therefore the above supposition appears to be disproved.

3. Induction (Nucleation) and Growth Periods

The study of both the induction and growth periods for barium sulfate precipitation was undertaken. Fresh and aged barium chloride solutions were mixed with sodium sulfate solutions. The sodium sulfate solutions were 5 x 10^{-4} molar, adjusted to a pH of 1.0. The barium chloride solutions were 0.05 molar and a twenty percent excess was used. The precipitation rate was followed by turbidimetric measurements with a Beckman Model B spectrophotometer; per cent transmission was plotted as a function of time after mixing of the solutions. Typical

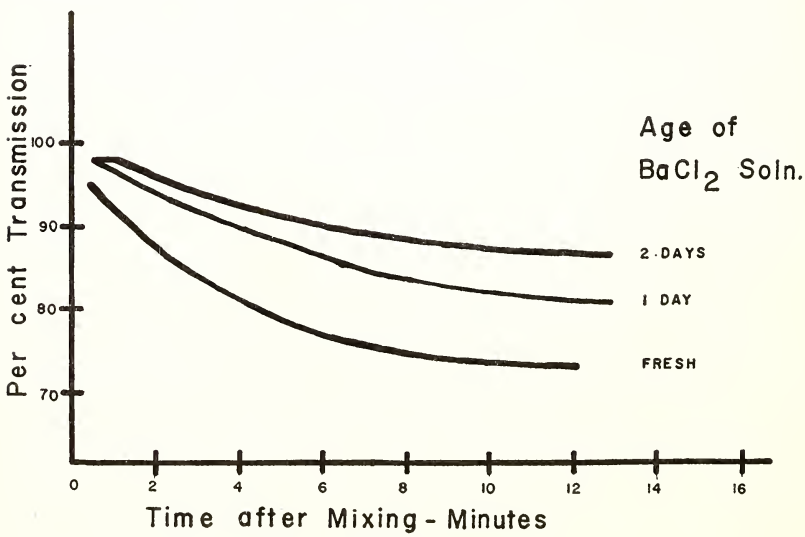

Figure 2.

curves are shown in figure 2. Each curve represents data obtained with a barium chloride solution of a certain age.

The final points of each curve indicate the relative particle sizes of the precipitates; the lower the per cent transmission, the smaller the particle size. The length of the growth period and the rate of growth appear to be constant. Assuming that nucleation occurs only during the induction period, and noting that the length of the induction period increases with the age of the barium chloride solution, we conclude that a fresh solution either nucleates at a faster rate than an aged solution or that there are initially excess nuclei in the fresh solution. It must be noted, however, that this experiment was conducted with extremely dilute solutions. With more concentrated solutions the nucleation period is so short that no measurements of its duration can be made by this method.

4. Effect of Adsorbents During the Aging Period

Adsorbents were kept in contact with barium chloride solutions during aging, and their effects on the particle size of barium sulfate were determined. Fresh solutions of 0.02 molar barium chloride were prepared containing glass wool, a porcelain crucible, or clay boiling chips. After known aging periods, portions of each solution were removed and added with shaking to a 0.016 molar sodium sulfate solution of pH 1.0. Particle sizes of the resulting precipitates were measured micro-

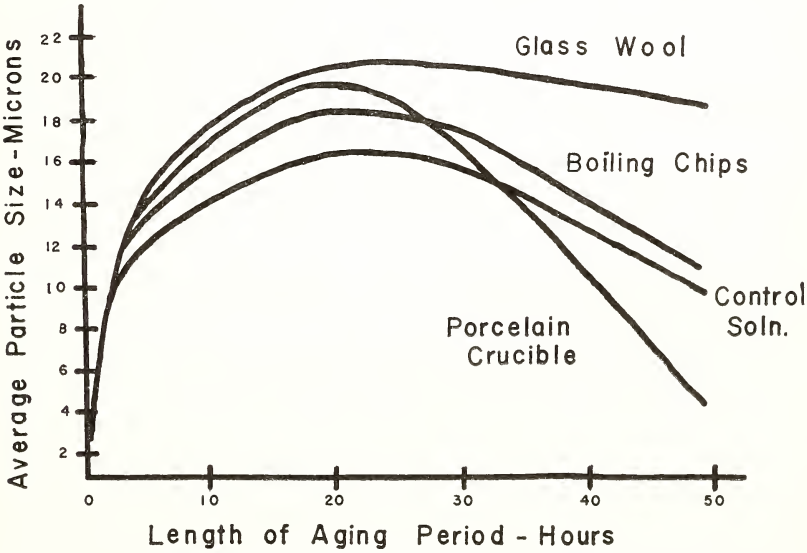

Figure 3.

scopically. Figure 3 is a plot of average particle size versus length of aging period. As indicated, the solutions containing added adsorbents produced larger particles for a comparable aging period than a control

solution. Glass wool, having the greatest surface area, produced the largest particles. The trend to smaller size again after long aging is shown by the maxima in all the curves.

5. Experiments With Radioactive Barium

In order to investigate Bogan's proposal that filtration removes undissolved barium chloride particles from a fresh solution by adsorption, radioactive barium was employed. Ba^{133} in the form of barium chloride was used as a tracer in filtration experiments with fresh and aged solutions. These experiments were performed both with Selas #3010 filtering crucibles and with Whatman #43 filter paper. Ten solutions of 0.02 molar barium chloride, partially active, were prepared for each filtering media. After known aging periods each solution was filtered through one of the media. The filtrates were evaporated, filter papers and crucibles dried, and the original beakers rinsed and dried. The activities of each were then counted with a Nuclear Instrument and Chemical Corporation Model 163 scaling unit. Ratios of activity of filter to activities of filter plus filtrate, and of activity on the walls of the beaker to total activity were calculated. The data are summarized in Table 1.

TABLE 1

Activity Ratios for Filtration Experiments with Barium Chloride Solutions

Sintered Porcelain Crucible								
	Length of Aging Period before Filtration							
	0	30 min.	1 hr.	3 hrs.	7 hrs.	20 hrs.	45 hrs.	78 hrs.
Act. of filter / Act. of filter plus filtrate	.0825	.0825	.0806	.0872	.0880	.0790	.0843	.0770
Act. of beaker / Total activity	.0204	.0299	.0296	.0422	.0362	.0454	.0662	.0578
Filter Paper								
	0	1 hr.	14 hrs.	42 hrs.	61 hrs.	110 hrs.	1 week	
Act. of filter / Act. of filter plus filtrate	.260	.244	.231	.257	.239	.250	.243	
Act. of beaker / Total activity	.0051	.0076	.0051	.0076	.0125	.0066	.0090	

Statistics indicated no significant difference in the ratio of activity of filter to activities of filter plus filtrate for different aging periods. This was construed to indicate the absence of any detectable, undissolved barium chloride particles in a fresh solution, since if such were the case these ratios would be greater for a fresh solution than for an aged one. The increase in the ratio of activity on the walls of the beaker to total activity, with aging, particularly in the experiments

with sintered porcelain crucibles, indicates an increased adsorption of barium ions on the walls of the container.

6. Other Solution Aging Effects

Investigation of the aging phenomenon was carried out with other solutions and precipitates. Slight, but real increases in particle size with age of the solution were noted for the following: (1) barium chloride in the precipitation of barium carbonate, (2) strontium chloride in the precipitation of strontium sulfate and strontium carbonate, and (3) barium nitrate in the precipitation of barium sulfate. No aging effects were found for: (1) barium chloride in the precipitation of barium chromate, (2) lead chloride in the precipitation of lead sulfate, and (3) calcium chloride in the precipitation of calcium carbonate. None of the effects were as pronounced as with aged solutions of barium chloride in the precipitation of barium sulfate.

Conclusion

Filtration of barium chloride solutions before aging appears to accelerate the complete cycle of the aging process.

With mixed solutions of fresh and aged barium chloride small barium sulfate particles are always produced, which seems to indicate the presence of excess nuclei in a fresh solution.

A fresh barium chloride solution may nucleate at a faster rate than an aged one, or the increased induction period on aging may also be due to the absence of excess nuclei initially present in a fresh solution.

Adsorbents kept in contact with barium chloride solutions during aging result in larger particles of barium sulfate than those produced from solutions aged without adsorbents.

Experiments with radioactive barium indicate the absence of any detectable, undissolved barium chloride particles in a fresh solution which could act as excess nuclei.

Although some other solutions exhibit aging effects, none are as pronounced as with barium chloride in the precipitation of barium sulfate. There appears to be no correlation between solutions which exhibit these effects.

It has been repeatedly shown that the particle size of barium sulfate is influenced by the age of the barium chloride reagent solution. The age of the sulfate reagent solution is of no effect. Since particle size depends on the number of nuclei available for particle formation, there must be more of these nuclei in a precipitate formed from a fresh solution than from an aged one. It is not clear what portion of the nuclei developed spontaneously during precipitation, and what portion must be present in the reagent solution. It is further not clear what any foreign nuclei in the barium chloride solution consist of, but it appears that they are not undissolved barium chloride particles. Probably nuclei coming from other sources, such as the walls of the container, play an important role. Experiments with other solutions which exhibit this phenomenon would be of value. The use of other techniques, such as polarography, which are not feasible with barium chloride solutions should yield important information.

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