The Absorption of Iron by Platinum Crucibles in Clay Fusions.

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A short time ago on making a number of clay analyses, we were surprised at the persistent gain in weight of our platinum crucibles and the repeated appearance of ferric oxide after reheating a crucible that had been used in making a fusion. No note of such phenomena could be found in the standard treatises on analytical chemistry at hand, no mention of the absorption of iron by platinum being mentioned by Fresenius, Treadwell and Hall, Olsen, Morse, or Scott. The only mention of such action to be found in the literature available was in a paper by Sosman and Hostetter, Jour. Washington Academy, 5, 293-303, and only a synopsis as given in Chem. Abstracts, 9, 1580, was at hand. In this paper account is given of experiments made on the heating of hematite and magnetite in platinum crucibles at high temperatures, resulting in the absorption of iron and the loss of oxygen. The statement is made that it is a generally known fact that platinum crucibles will absorb small quantities of iron when heated to high temperatures with ferric oxide. In this synopsis in Chemical Abstracts no reference is made to any published data.

If a sample of ordinary clay is mixed with the usual amount of sodium carbonate and the mixture fused in the usual manner, the crucible will present the appearance of perfectly clean platinum when the product, on cooling, is removed by the treatment with hydrochloric acid. If this crucible is now heated for several minutes over the blast lamp or No. 3 Meeker burner, the lower third of the inside of the crucible will have an appearance varying from that of ordinary ferric oxide to that of certain bronzes. If strong hydrochloric acid is now added and the crucible heated gently, what appears to be a rather strong solution of ferric chloride is obtained. If this is removed, the crucible will have again the appearance of clean platinum, but, in many cases, when heated a second time, more iron will be driven to the surface and converted into ferric oxide. In some cases it has been found

necessary to subject the crucible to several successive heatings and treatment with strong hydrochloric acid in order to remove all of the iron absobed in a single fusion.

In order to determine whether this amount of iron is what might be considered merely a "trace" or whether it is sufficient to make an appreciable difference in the results of a quantitative analysis, several determinations were made. A platinum crucible was heated to constant weight after it had been subjected a number of times to the treatment just mentioned. A clay fusion was then made and the product removed by the aid of 20 per cent hydrochloric acid. The heating and treatment with the acid was then repeated until no further change was observed. The combined solutions of ferric chloride was reduced with stannous chloride, excess of mercuric chloride added, and the amount of iron determined by means of a standard solution of potassium dichromate. Some of the results obtained are as follows:

Weight of platinum crucible (from previous fusion) after successive heatings over an ordinary burner:

25.0089 25.0089 25.0090 25.0089

Same crucible after successive heatings of fifteen minutes each over a Meeker burner:

25.0097 25.0097 25.0095 25.0097

After treatment with the acid and complete removal of the iron:

25.0089 25.0090 25.0090 25.0089 25.0089

A fusion of a mixture of 0.5 gram of clay and 2.5 grams of sodium carbonate was then made and the product removed by the aid of the acid. Successive heatings over the Meeker burner, each followed by removal of the iron present, left the crucible weighing as follows:

25.0099 25.0097 25.0099 25.0103

After removal of the iron successive heatings gave

25.0089 25.0084 25.0088

After further treatment with the acid and successive heatings, the weights ran as follows:

25.0084 25.0083 25.0084 25.0081 25.0081 25.0082

The total amount of iron oxide found by titration with the potassium dichromate was 0.00459 gram.

After a third fusion, removal of the product, and heating over the Meeker burner the crucible weighed

25.0097 25.0098

After removal of the ferric oxide and reheating,

25.0080 25.0080 25.0080 25.0080

Amount of ferric oxide by titration, 0.0063 gram.

After a fourth fusion, removal of fusion product, successive heatings gave

25.0103 25.0100 25.0100

After removal of the iron oxide,

25.0085 25.0085

Total amount of ferric oxide by titration, 0.0051.

It seems that in fusing the clay and sodium carbonate mixture a very small amount the ferric oxide formed, or the ferrous oxide present is reduced, the iron dissolving in the platinum. When the crucible is afterwards heated to a high temperature, the iron is driven to the surface and reoxidized, thereby becoming soluble in the acid.

It was thought that this might be prevented by adding a small amount of potassium nitrate to the fusion mixture before making the fusion. A few experiments were made to test this hypothesis.

Weight of the crucible before fusion, 25.0079.

To the mixture of 0.5 gram clay and 2.5 grams sodium carbonate was added 0.3 gram pure potassium nitrate, the fusion made and the product removed in the usual way. The crucible was then heated eight times, fifteen minutes each, and weighed after each heating, the ferric oxide being removed before the succeeding heating. The weights were as follows:

25.0104 25.0103 25.0103 25.0103 25.0091 25.0087 25.0079 25.0079

The total amount of ferric oxide obtained by titration, 0.0021 gram.

A second fusion with the addition of 0.5 gram of potassium nitrate brought the weights of the crucible to the following:

25.0125 25.0122 25.0121 25.0120 25.0120 25.0120

The total amount of ferric oxide by titration, 0.0015 gram.

A third fusion, using again 0.5 gram of potassium nitrate resulted in the following weights:

25.0154 25.0152 25.0149 25.0149 25.0149 25.0149

No ferric oxide was detected by titration although a trace of ferric oxide was observed in the crucible.

A fourth trial with 0.5 gram of the nitrate resulted as follows:
25.0182 25.0181 25.0181 25.0178 25.0170 25.0165 25.0165
Total amount of ferric oxide by titration, 0.0025 gram.

It will be seen that the amount of iron absorbed by the crucible is sufficient to be taken into account in making an accurate analysis. In other words, after making a clay fusion, the crucible should be heated to a high temperature and the ferric oxide formed dissolved out and added to the vessel containing the main fusion product. Furthermore, it is seen that treatment with potassium nitrate is not a satisfactory way of avoiding the trouble, for while it does prevent the absorption of the iron to a large degree, it is the means of introducing other foreign substances into the crucible which may prove undesirable.

That this absorption of iron is not a peculiarity of this particular crucible, due to the presence of some other metal alloyed with the platinum, would seem to be indicated by the fact that the same phenomenon was observed in connection with two other crucibles purchased at different times and from different dealers; that it was not due to some unusual property of this particular clay is evidenced by the fact that the same thing occurred with clays obtained from widely different sections of the State.

A further study of this behavior is in progress.

Since the above paper was submitted for publication, the chief cause of the phenomena described has been discovered. The crucibles in which the fusions were made were heated over Meeker burners. In order that they might be heated to the highest temperature obtainable from these burners the crucibles were supported just above the top of the burners. As a result they were more or less enveloped in an atmosphere of reducing gases and it was due to these gases rather than to the organic matter in the clay that the iron was brought to a condition to be absorbed by the platinum. When these fusions are made with a good blast

lamp directed upon the crucible at a considerable angle, practically no iron is afterwards found in the platinum. It is probably because these burners have not generally been used for this purpose that this phenomenon has not been observed by others. It is clear that the Meeker burner is not a satisfactory substitute for the blast lamp in making fusions of clays or silicates that contain appreciable amounts of iron.