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CORROSION OF METALS IN URANYL SULFATE SOLUTION

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SUMMARY

^{Pb} ~~Lead~~ is seriously attacked at 100°C in 0.1 N H₂SO₄ containing up to 4 gm U/liter as ~~uranium~~ ^{UO₂SO₄}, the attack increasing with the ~~uranium~~ ^{UO₂SO₄} concentration. In the range 0.5-1.0 N H₂SO₄, the corrosion product accumulated on the specimen. A protective film appeared to form on ~~lead~~ ^{Pb} in 1 N H₂SO₄ at 70°C during a 15 day exposure. A somewhat thicker film was formed when the solution also contained 10⁻³ N H₂O₂.

^{UO₂} ~~Columbium~~ was very resistant to corrosion under the conditions studied. *end*

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Among the metals resistant to sulfuric acid and suitable from the neutron absorption point of view there are only two, namely, lead and columbium.

Columbium is quoted as being resistant to sulfuric acid at all concentrations. Only hot concentrated acid leads to a slow attack.⁷

The solubility of lead in sulfuric acid depends on the degree of purity of the metal. For a given metal its resistance to H_2SO_4 depends on the concentration and the temperature of the acid.

The effect of various impurities on the corrosion resistance of lead in sulfuric acid may be summarized in the following way:

Sb: The presence of Sb up to 0.2% has little or no harmful effect; higher proportions are, however, inadmissible, especially for metals intended for contact with hot concentrated acid.¹

Cu: More than 0.2% Cu is injurious to lead but between 0.1 and 0.2% copper has no appreciable effect on the resistance to cold acid; above 200° Cu has a protective action on lead reducing its chance to being converted to sulfate up to 240°C.²

Ag, As, S and Sn: These elements increase the corrosion resistance of lead.³

Zn: Zinc in small proportions accelerates the action of the acid more than the other metals.⁴

¹Lunge and Weibel, Chem. Ind., 9, 47, 1886.

²Hale and Foster, J. Soc. Chem. Ind., 34, 464, 1915.

³Bans, J. Soc. Chem. Ind., 38, 407, 1919.

⁴Rowell, J. Soc. Chem. Ind., 39, 235, 1920.

⁵Jones, J. Soc. Chem. Ind., 39, 221, 1920.

⁶Lancaster, J. Chem. Ind., 38, 408, 1919.

⁷Mellor, Inorganic Chem.

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Bi: Bismuth like zinc favors corrosion of lead in sulfuric acid. However, if Bi and Sb are present together they neutralise the action of each other.³

Hg: Hg has a very harmful effect on the corrosion resistance of lead.⁵

Electrolytic lead 99.998% resists the action of concentrated H_2SO_4 up to $310^\circ C$.⁶ The effect of concentration and temperature has been studied by various authors, but the data do not coincide, probably because the experiments were run with metals of different degrees of purity.

However, for any given case it appears that the corrosion rate increases very slowly with the concentration up to about an acid of specific gravity of 1.8 after which it proceeds much more rapidly. The temperature effect is relatively unimportant. The corrosion rate starts to rise at temperatures above $150^\circ C$. The presence of oxygen seems to favor the attack by H_2SO_4 .⁸ On the other hand, it was found that lead in dilute sulfuric acid is not corroded when in presence of H_2O_2 .⁹ These results lead us to think that either columbium or lead would be resistant to uranyl sulfate solutions. However, the role of heavy metal in the corrosion by the acid is unknown and therefore a few experiments were undertaken in order to determine the effect of the heavy metal concentration in acids of different normalities.

The study is separated into three different parts;

1. Study of the effect of heavy metal on corrosion resistance of Pb and Cb in UO_2SO_4 .
2. Determination of the corrosion rate of these two metals in 1 normal H_2SO_4 solution containing 3 gr. of heavy metal per liter.
3. Effect of H_2O_2 on the corrosion resistance of Pb and Cb in the defined solution in 2.

⁸Whitman and Russel, J. Ind. Chem., 17, 348, 1925.

⁹Salnowsky, Che. Ztg., 40, 449, 1916.

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I. Effect of Heavy Metal on Corrosion Resistance of Pb and Cb in H_2SO_4

Experimental Technique: Samples were cut out of a sheet. They were 1.27 cm. wide, 6.35 cm. long, 0.165 cm. thick for lead, and 1.6 cm. wide, 1.6 cm. long, and 0.096 cm. thick for columbium. They were cleaned in carbon tetrachloride and weighed.

The samples were then introduced in round flasks filled with uranyl solutions. Reflux condensers were fixed on the flasks, and the solutions were allowed to boil for a period of 40 hours.

After that the samples were rinsed and brushed with a smooth brush, dried, and weighed.

Results:

Lead: The results achieved are represented by the graphs of Fig. 1. One may see that lead is dissolved in 0.1 N solutions at a rate increasing with the heavy metal content. For 0.5 N solution the loss of weight occurs only for the solution having 1 gr./liter of heavy metal, a gain of weight takes place for higher concentration of heavy metal.

In one normal sulfuric acid, no reaction takes place when the content of heavy metal is of 1 gr/liter. The gain of weight corresponding to higher concentration of heavy metal is approximately the same for 3 gr. as for the 2.5 gr. heavy metal containing solutions.

It seems that the heavy metal catalyses the formation of the initial product of corrosion. In the conditions of the electrolyte where the product is soluble, the presence of the heavy metal leads to acceleration of corrosion while in the conditions of the electrolyte where the product of corrosion is insoluble, it hinders the attack.

However, these results correspond to a 40-hour period, and it is necessary to determine the behavior of the surface film over a longer period of time, and establish the effect of the time factor.

Columbium: No change of weight could be detected in any of the solutions.

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II. Corrosion Rate of Lead in a Uranyl Solution Containing 3 gr. of Heavy Metal per Liter of One Normal Sulfuric Acid.

Experimental Technique: The samples were of the same dimensions as in the previous studies. They were suspended in gas washing bottles filled with the solution and placed in an automatically controlled thermostat at 70°C. After having remained in the solution for a given period of time the samples were taken out, brushed, rinsed, and dried.

Results:

Lead: All the samples, after being in contact with the corrosive media, were covered with a very adherent gray coating which could not be removed with a brush; it cannot be scratched with the nail. The graph of Fig. 2, represents the gain of weight as a function of time. The curve obtained is characteristic of a "self-protecting" mechanism. The gain of weight corresponds to the formation of a surface film. When the entire surface is covered, the reaction between the metal and the corrosive medium stops, the surface film providing a complete protection. The thickness of the film is extremely low since a maximum gain of weight corresponds to 2 mg/cm².

One may assume that lead in presence of uranyl sulfate solution (3 gr./liter of 1 normal sulfuric acid) develops a protective film which shields the metal against any further reaction. The adherence of the film is very good so that no chipping off may be expected. The effect of H₂O₂ was studied in the following conditions.

III. Effect of H₂O₂ on Corrosion Resistance of Lead in Uranyl Sulfate Solution.

The technique used was the same as for the previous experiments. In order to maintain H₂O₂ at the concentration of 10⁻³ N, a strong H₂O₂ solution was fed into the corrosive medium to insure constant concentration, which was periodically checked.

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After various periods of exposure the samples were taken out, brushed, rinsed, and weighed.

Results:

The appearance of the samples after the test is the same as that of the samples corroded in H_2O_2 free uranyl sulfate solutions. The samples are covered with a gray adherent film. The graph of the figure 2 represents the gain of weight of lead. One may see that in the presence of hydrogen peroxide, the coating formed is somewhat thicker, due probably to a different type of oxide formed. The gain of weight with time, high at the beginning of the experiment, shows that the coating once reaching its maximum thickness protects the metal against further oxidation.

These results seem to imply that the presence of hydrogen peroxide in the uranyl solution leads to the formation of a surface coating, the thickness of which is slightly higher than that formed in an H_2O_2 free solutions.

Columbium: No change in weight could be detected after 15 days of exposure to the H_2O_2 containing uranyl sulfate solution.

Conclusion:

The results described here lead to the conclusion that either lead or columbium can be used as structural material. In the case of lead, a protective coating is formed, as a result of the insoluble product of corrosion. This surface coating once formed prevents the metal against any further reaction. The adherence of the coating is such that it cannot be peeled away by any mechanical means.

In the case of columbium no reaction between the metal and the corrosive medium takes place.

The results given here should be considered only as an indication of the general behavior of the metal. It has to be borne in mind that a slight change in the conditions will lead to a change in the absolute value of the results.

If one of these metals should be considered for the construction, it would

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be advisable to repeat the experiments in conditions as close as possible to the working conditions, since the exact mechanism of corrosion of lead in uranyl sulfate solution could not be studied due to the lack of time and personnel.

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SOLUTION RATE OF Pb IN $\text{UO}_2 \text{SO}_4$

. — = 0.1 gr of U per liter

o - - = 2.5 gr " " " "

x — = 4 gr " " " "

Temperature: 100°C
Time: 40 hours

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CORROSION RESISTANCE OF LEAD IN URANYL SULFATE SOLUTION
CONTAINING 3 GR OF HEAVY METAL PER LITER
OF ONE NORMAL SULFURIC ACID

—•— without H_2O_2
—x— with $10^{-3}N H_2O_2$

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