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Chem 3-315
July 23, 1947

RL-4.6.315

The Electrolytic Reduction - pH Control Method of Separation
of T from Contaminants

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Recent consideration of the electrolytic means of reduction in conjunction with the pH-control method of separation has led to this preliminary report.

The electrolytic reduction, as now employed, is carried out on an acid chloride solution in a water-jacketed glass cell with an agitated mercury pool cathode and a graphite anode. The anode is surrounded by a porous alundum cup which prevents the liberated chlorine from contacting the tuballoy ion and reoxidizing it to tubanyl ion. This cell, using a current density of 0.3 ampere per square centimeter at ten volts, reduces about 60 grams of tuballoy, in a 5 percent solution, per hour. Another cell, now in the process of development, built of different geometry for continuous operation will, at the present time, reduce between 500 and 600 milliliters of 5 percent tuballoy solution (25 to 30 grams of tuballoy) per hour with a current density of about 0.1 ampere per square centimeter at 3.5 volts. The solutions from these cells will contain varying amounts of trivalent tuballoy, up to 25 percent in the batch reductions and 1 to 5 percent in the continuous operating cell.

The pH-control method of separation in this case consists of adjusting the pH to the value to be used on the reduced chloride solution of the metallic constituents. The solution will consist mainly of tuballoy ion, ferrous ion, chromic (and chromous) ion, nickelous ion, with smaller amounts of trivalent tuballoy, copper, manganese, molybdenum, etc., all mainly as the chlorides.

Previous experience with this method has shown that chromium will not be separated under these conditions of precipitation at pH 4.5. It was hoped that precipitation at a low enough pH could be used such that a good tuballoy recovery might be obtained and that the majority of the chromium would remain in the filtrate. The loss of tuballoy from a 4 percent solution precipitated at pH 3.5 is 0.8 percent, at pH 4.0 the loss is .02 percent, and at and above pH 4.5 the loss is not detectable by gravimetric means of analysis for tuballoy. (cf. Figure 1) Apparently, then, it is possible to lower the precipitation pH without too great a tuballoy loss. The precipitate obtained at and below pH 3.0 at room temperature is so unfilterable that not enough filtrate could be obtained for analysis. The filtration time at pH 3.5 is seven times that at pH 4.5 and three times greater than at pH 4.0 with precipitations at higher pH values even shorter filtration times are obtained. (cf. Figure 2, curve A) Heating such precipitates appears to give a less hydrated and more filterable form and it may be that the filtration difficulty can to a large degree be eliminated by this means. However, when 'gunk' solutions are precipitated at these lower pH values, the precipitate obtained is considerably more filterable than with tuballoy solutions alone (cf. Figure 2, curve B).

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143-1

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Synthetic 'gunk' solutions containing 5 percent tuballoy, 0.2 percent iron, .05 percent nickel, and .02 percent chromium as tuballoyous, ferrous, nickelous and chromic chlorides when adjusted to pH 4.0 and pH 5.0 contained in the unwashed precipitates the following proportions of the original constituents:

Precipitated at pH 4.0

tuballoy....	99.0 percent
chromium....	100 "
iron.....	20 "
nickel.....	15 "

Precipitated at pH 5.0

tuballoy....	99.9 percent
chromium....	100 "
iron.....	18 "
nickel.....	14 "

Another wash with hot dilute ammonia would have removed most of the remaining nickel.

The presence of so much iron in the precipitate seems to be due to partial air oxidation of ferrous to ferric hydroxide. Tuballoyous ion, when tied up as the hydroxide, apparently will not keep the iron reduced and a scum of ferric hydroxide forms on the surface. Solutions containing 5 percent tuballoy and from 0.1 to 0.5 percent ferrous ion, when precipitated at pH 4.5, contained in the tuballoy precipitate from 30 to 5 percent of the original iron (cf. Figure 3). The iron in the precipitate seemed to be in the form of ferric hydroxide as in all cases a reddish-brown scum formed on the surface of the solution. The addition of 0, 0.1, 0.3, and 0.5 percent hydroxylamine to a 5 percent tuballoy solution containing 0.3 percent iron, reduced the iron content in the precipitate obtained at pH 4.5 from 10 to 9, 4 and 2 percent of the original, respectively. (cf. Figure A). The maximum loss of tuballoy occurred with the higher percent of hydroxylamine and was 0.1 percent.

It seems probable that the extra reducing power of the actual electrolytic solutions, which contain trivalent tuballoy, will be sufficient to prevent air oxidation of the iron and this appears to be the case. A solution containing 5 percent tuballoy and 0.25 percent iron electrolytically reduced until a few percent of the tuballoy were present in the trivalent form, contained only one percent of the original iron in the tuballoyous hydroxide precipitate obtained at pH 4.5. However, if the amount of trivalent tuballoy in the electrolytically reduced solutions is found not sufficient to keep the iron in the ferrous state when exposed to air, it may be necessary to add a small quantity of some other reducing agent such as ammonium hyposulfite or hydroxylamine. The possibility of keeping the solution out of contact with air while ammonia is being added should also be considered.

Synthetic 'gunk' solutions containing

5	percent tuballoy
0.4	" iron
0.15	" nickel
0.075	" chromium
0.05	" copper

When separated by pH control and washed twice by slurring with 30 percent aliquots of two percent ammonium nitrate contained in the precipitate the following percentages of the constituents originally present:

Precipitated at pH 3.5

tuballoy..	96.0 percent
iron.....	0.0 "
nickel....	0.0 "
chromium..	82.2 "
copper....	0.0 "

Precipitated at pH 4.0

tuballoy..	99.0 percent
iron.....	0.0 "
nickel....	0.0 "
chromium..	95.5 "
copper....	0.0 "

Precipitated at pH 4.5

tuballoy..	99.6 percent
iron.....	0.0 "
nickel....	0.0 "
chromium..	98.8 "
copper....	0.0 "

SECRET 3

Apparently then, chromium cannot be separated from tuballoy by pH control as now used even at comparatively low pH values. If a means could be found for effectively tying up chromium in such a way that chromic hydroxide will not precipitate (or that the tuballoy chromite will not form), then it may still be possible to effectively use the pH control method of separation.

Chromium shows a great tendency to form complex ions with hydrocyanic and sulfuric acids, organic compounds containing hydroxyl, and with ammonia, amines, pyridine, etc., and these complex compounds do not show many of the characteristic chromium reactions. Cyanide apparently does help to some extent, but in the preliminary trials 40-50 percent of the chromium still remained in the tuballoy precipitate. Most other compounds which form strong enough complexes with chromium to prevent the hydroxide from precipitating also form precipitates and complexes with tuballoy ion. In this group can be included tartaric, citric, and oxalic acids, and sulfites. Sugar, with which it is claimed chromic hydroxide will not precipitate, could not be made to prevent precipitation even after boiling. However, this type of complex forms slowly and it may be that the complex was never formed.

It appears then, that the pH control method cannot be used for complete separation until the chromium problem has been solved.

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per S.S.C.R.

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compiled by E.L. Wagner