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SEPARATION OF COPPER FROM OTHER METALS

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This invention relates to the separation of copper from alloys or other mixtures of the same with one or more metals electropositive to copper. More specifically, the invention relates to separation of copper from scrap alloys or other mixtures containing copper, such as for example, copper-nickel scrap (e. g. Monel, nickeline, constantan, etc.), and is applicable to alloys or other mixtures of copper with, among other metals electropositive to copper, aluminum, manganese, beryllium, zinc, iron, cadmium, cobalt, nickel, antimony and tin. The alloy may contain copper and any one or more of the other metals named. It may also contain, in addition to the above metals, minor amounts of elements not electropositive to copper, which, providing the alloy as a whole is electropositive, do not affect the basic reactions. However, such elements may, because of the insolubility of their compounds or the formation of inert coatings on the metal, eventually inhibit the reaction unless special means, differing with the circumstances, are used to prevent such formation. These special means affect only those elements in the alloy which are not electropositive to copper and, therefore, do not affect the general procedure which constitutes this invention.

I have discovered that if a reaction mixture comprising a body of an alloy or other mixture of the class stated, an aqueous acid solution containing ions of the class consisting of chloride and sulfate or both and finely divided sulfur is heated, the copper content of the alloy or other mixture, together with the copper in solution, if any, is converted to copper sulfide while the more electropositive metal or metals go into solution to form their salt or salts, sulfur and free acid in the solution being used up in the reaction. Not only does the free acid in the solution combine with the more electropositive metal or metals, but the negative ion released by reaction of the copper salt in the solution with sulfur to form copper sulfide reacts with the more electropositive metal or metals to form the soluble salt. Thus, neglecting possible intermediate reactions, there are three simultaneous reactions going on, viz., first, the sulfur reacts with the copper at the surface of the metal to form copper sulfide which immediately precipitates, second, the more electropositive metal reacts with the negative ions present to form a solution of the salt or salts, and third, the sulfur reacts with any copper salt in solution throwing down copper sulfide and setting free negative ions for the reaction with the more electropositive metal or metals.

Disregarding side reactions, which in some instances cause loss of sulfur as hydrogen sulfide, the several factors can be approximately balanced, thus, the amount of sulfur can be approximately such as required to react with all copper in the solution initially, and all the copper to be released from the alloy as the more electropositive constituents dissolve. The amount of free acid can be such that its negative ion plus the negative ion associated with copper initially in solution will be approximately such as required to dissolve the electropositive metal. The amount of alloy or other mixture of metals theoretically required to remove all copper from solution is such as to supply to the solution electropositive metal or metals in quantity molecularly equivalent to the compounds furnishing the negative ions in the solution.

Since, practically, the composition of the alloy will always be known, the other factors can be calculated in advance so that at the end of the reaction there will be left in the reaction vessel only a copper free solution of the salt or salts of the electropositive metal or metals and a dense and easily filterable precipitate of copper sulfide.

This balance may be the preferred practice but, as shown by some of the examples, considerable deviation from a balance does not interfere with the reactions and may be considered satisfactory practice. For instance, if the metals are in the form of powder or very finely divided, or as thin scrap or fine wire, a balance as above would probably be preferred. However, if the metals are in the form of coarse or heavy scrap, a countercurrent process might be preferred in which excess metal would be present at the end of each batch, this method shortening the reaction time by making available a larger amount of metallic surface. One of the advantages of the method is that the copper sulfide does not adhere to the excess metal so that during the reaction the metal surfaces are always relatively clean and reactive, and at the conclusion of the reaction, the excess metal may be readily separated from the copper sulfide precipitate. The remaining metal has essentially the composition of the original metal, being neither substantially enriched by copper nor substantially depleted of the more electropositive metal or metals.

In practice, the sulfur would be kept as low as possible but a slight excess over theoretical requirements would probably be preferred to insure complete reaction and to maintain a rapid reaction rate up to the end.

The amount of free acid may be adjusted from only that required to prevent the precipitation

of basic salts to an amount sufficient to furnish a considerable proportion of the negative ion, in fact, as hereinafter explained, if no copper salt is in solution initially the acid can furnish the entire amount of negative ion.

In the practical operation of the process, there are some slight divergences from theoretical results but they are not of great importance. For example, some metal and some free sulfur are frequently found in the precipitate and the composition of the copper sulfide itself may vary between cupric sulfide and cuprous sulfide.

While the result is the same in each case the chemical reactions involved seem to be several, the importance of each of which varies according to the acid and metal employed. When metals highly electropositive to copper are employed, more or less metallic copper is thrown out first, this then reacting with sulfur to form copper sulfide. If copper is thrown out as an adherent coating, the rate at which it is thrown out will be increasingly slower until the sulfur has combined with it when the two reactions seem to proceed at a balanced rate. When the metal is not so greatly electropositive, the combination of sulfur and copper may take place at the surface of the metal without visible evidence of intermediate stages. If copper is present in the solution at the start and is in the form of the chloride, there may be reduction first followed by the formation of the sulfide at some distance from the metal surface. However, if cupric sulfate is present in a wholly sulfate solution, the same formation of sulfide still occurs. There is frequently more or less formation of hydrogen sulfide, the amount being, apparently, somewhat dependent upon the metal employed and upon the rate of addition of the sulfur to the solution. The precipitation of copper by H_2S, at least to some extent, seems likely.

The process, as described thus far, presupposes that the initial reaction mixture contains in solution salts of the constituent metals of the alloy. This is not essential. If the initial mixture conains merely the alloy, water, sulfur, and acid, the copper from the alloy will react with the sulfur while the more electropositive metal or metals will dissolve. After a short interval of operation, the reaction mixture will contain all the components as in the previously described batch, except that there will be at no time any considerable concentration of copper in solution. It is, then, clear that copper in solution is not necessary unless it be supposed that it dissolves momentarily before reacting with sulfur. In any event, no substantial concentration of copper salt in solution is essential.

This method is applicable to separating copper and more electropositive metals which are not alloys. Examples of such use would be the separation of a mixture of metallic powders or finely disseminated metals in a non-metallic matrix such as might be obtained by in situ or gaseous reduction of an ore, one of the powdered metals or disseminated metals being copper, and the others more electropositive. By heating such a mixture of metals with acid (or a suitable metallic salt), water, and sulfur so that the copper is precipitated as copper sulfide and the more electropositive metals are put into solution, the essentials of this invention in its broad aspect have been complied with.

The negative ions preferred are the chloride ion, the sulfate ion, or a mixture of the two, but I may make use of other negative ions which do not exert a solvent action on copper sulfide and which do not precipitate the other metal as an insoluble salt.

While I prefer to employ finely ground or flowers or sulfur, the sulfur need not be in this form. I have also used other forms of sulfur including small lumps or as when the boiling point of the salt solution is above the melting point of sulfur, the latter is used as an emulsion of melted sulfur. I have also added in many cases a small amount of wetting agent to prevent agglomeration and floating of the finely powdered sulfur. This is not necessary, nor is there any catalytic effect to be gained by the wetting agent. The reaction proceeds without this addition, and with proper mixing of the sulfur in a small portion of acid or acid and strong salt solution its weting may be accomplished.

A typical utilization of the process would be in the treatment of a copper-nickel scrap, such as Monel. This scrap can be dissolved to form a mixed and very concentrated slightly acid solution of, for example, the chlorides, of nickel, copper and smaller amounts of other metals. This can be done by known methods which form no part of the present invention. This concentrated solution of the chlorides can then be heated with more of the scrap and elemental sulfur during which the copper can be completely removed as the sulfide and replaced by an equivalent amount of nickel so that the solution is now copper free and is as concentrated with respect to nickel as it was originally with respect to nickel and copper combined.

It is possible to utilize copper-nickel scrap, such as Monel, by my process without starting with an initial mixed chloride solution; the scrap may be dissolved in HCl in boiling solution while sulfur is present. Thus, all the conditions of the process are fulfilled by boiling sulfur, HCl and water together in the presence of the scrap. HCl under these conditions, and particularly after some $NiCl_2$ concentration has been built up, rapidly attacks the metal whereupon copper sulfide is precipitated and nickel enters the solution as nickel chloride. This makes apparent a further advantage of my invention, namely that disintegration of alloys relatively resistant to ordinary acids is accomplished comparatively easily.

I have tried precipitating the copper as metallic copper from mixed chloride solutions of copper and nickel by the use of an alloy of copper and nickel (using no sulfur). The approximate composition of the alloy was 67% Ni and 30% Cu, and the ratio of copper to nickel in the solution was approximately the same. This method fails due to the formation of an adherent and relatively insoluble coating of copper on the alloy making it necessary to use very large quantities of alloy to gain a completely copper-free solution. It also increases the copper content, by virtue of the copper plate, of the residual alloy, thus a further treatment by known methods of this residual alloy will give a solution relatively higher in copper and because of this increase in the circuating load of copper eventually there will come a time when a large amount of nickel must be sacrificed to eliminate copper. The known method of removing copper from mixed solutions by precipitation on iron or some similar metal merely changes the impurity copper for a like amount of impurity of the metal employed unless, of course, the metal wanted in solution can be used, which is often uneconomical. The known method of removing copper by

means of H_2S is often inconvenient or costly, leaves a solution relatively weaker in respect to the soluble other metal than the method which I propose and may even fail when the other metal is one which is also precipitated by H_2S in acid solution.

It is also apparent that the two foregoing methods may be effectively combined, i. e., for example, starting with a mixed chloride solution containing copper and nickel as obtained by known methods, copper nickel scrap can be added together with sufficient sulfur to combine with the copper from the solution and with that from the scrap that disintegrates in the process. The solution, after an interval of heating, will contain nickel chloride and no copper chloride. To this concentrated solution additions of HCl can be made together with further additions of sulfur and of scrap. Portions of the copper-free concentrated nickel solution and precipitated copper sulfide can be continuously or intermittently removed. The process can thus be maintained indefinitely.

Another application of this method would be a step in the recovery of cobalt from an alloy containing cobalt, copper and iron. A concentrated and slightly acid solution of the mixed chlorides of cobalt, copper and iron can be obtained by known methods. This solution may be boiled with sulfur and more of the original alloy in which process cobalt and iron enter the solution as chlorides in essentially the same ratio as they are present in the ore, while the copper in the solution originally as well as the copper released from the alloy is precipitated as copper sulfide. Thus is obtained a concentrated solution of cobalt and iron (from which the iron may be removed by known methods) and a precipitate of copper sulfide relatively free from cobalt and iron which may be treated by known methods to recover copper.

The following specific examples will serve to illustrate the invention:

Example I

The initial solution contained 400 cc. of liquid including 87 g. of nickel, 27.3 g. of copper and 1.72 g. of iron, all as chlorides. To this solution was added 50 g. of Monel metal and 15 cc. of concentrated HCl. About 15.5 g. of finely divided sulfur slurried in 50 cc. of water was then added, and the mixture boiled for 2 hours. It was found that 45.7 g. of the Monel metal had dissolved and 58.2 g. of copper sulfide precipitate (very dense and easily washed) was obtained. The solution contained 119 g. of nickel and only about 0.02 g. of copper. Essentially all of the iron remained in the solution. Contained in the copper sulfide precipitate was a small amount of free sulfur and 3.0 g. of nickel, 2.5% of the total nickel involved in the reaction.

Example II

50 g. of an alloy containing about 39.0% cobalt, 37.7% iron, and 15.0% copper was treated at boiling temperature with 358 cc. of 17.7° Bé. commercial hydrochloric acid added in successive portions and 20 g. of sulfur. Just enough water was added to maintain a pink rather than a blue solution. After 5 hours during which much of the HCl had been lost by boiling off, 49 g. of the alloy had been dissolved. Approximately 19.1 g. of Co and 18.5 g. of Fe had gone into solution which was free of copper, and only slightly acid, pH about 1.2. The copper sulfide precipitate weighed 28 g. and analyzed 26.2% Cu, 1.09% Co and 1.15% Fe. There was a large excess of sulfur.

Example III

50 g. of Monel scrap was treated at boiling temperature with 19 g. of sulfur in a boiling solution of 200 cc. water, 35.5 cc. of 95% sulfuric acid and containing initially 2.24 g. nickel as the sulfate. After 5 hours, 40.9 g. of the scrap had been dissolved enriching the solution which was copper-free with 27.7 g. of nickel. The sulfide precipitate weighed 23.0 g., contained approximately 53% of copper and some obviously unreacted sulfur. Included in this precipitate was 6.5% nickel, much of which was soluble by further digestion of the precipitate with fresh acid. A large amount, approximately half, of the sulfur was lost as hydrogen sulfide.

Example IV

The initial solution of 200 cc. contained 1.86 g. of sopper as cupric chloride and 20 g. of cadmium as cadmium sulfate, and 5 cc. of concentrated HCl. This was boiled with 1.0 g. of sulfur and an excess of cadmium metal. Metallic copper which first precipitated on the cadmium was rapidly replaced with copper sulfide which fell off the cadmium surfaces and to the bottom of the flask. The removal of the copper from the solution was complete in a short time. At the end, there was no metallic copper in the precipitate and the cadmium surfaces on the excess metal were clean.

Example V

The initial solution contained 1.86 g. of copper as cupric chloride and about 15.3 g. of antimony as antimony trichloride, and enough HCl to have a pH of 1.0. This was boiled with 5 g. of sulfur and an excess of metallic antimony. After 90 minutes the solution contained no copper and the black copper sulfide precipitate contained very little if any antimony.

Example VI

The alloy was scrap clippings of beryllium bronze containing 97% Cu and 2.5% Be. 8.48 g. of the bronze were heated together with 1.0 g. of sulfur flour and a solution of approximately 100 cc. containing 1.37 g. Be as chloride and a little free HCl. After about one and a half hours, 2.06 g. of the bronze had been disintegrated with formation of 2.51 g. of copper sulfide precipitate. The beryllium solution was copper free, and there had been some evolution of H_2S.

Example VII

An alloy known as constantan, containing about 60% Cu and 40% Ni was treated. 10.52 g. of the alloy was heated together with 0.5 g. of sulfur flour in a solution of about 100 cc. containing 0.37 g. Cu and 5.6 g. of Ni both as chlorides and a 0.5 cc. concentrated HCl. In a short time, 1.53 g. of the alloy had been used up, the solution was essentially copper free and 1.65 g. of copper sulfide precipitate had been produced as a fine powder.

Example VIII

3.38 g. of an alloy known as Manganin in the form of very fine gauge wire containing approximately 82–6% Cu, 4–15% Mn, 2–12% Ni and a little Fe was heated in a solution of about 100 cc. containing 0.18 g. Cu, 3.75 g. Ni and 4.7 g. of Mn all as chlorides, together with a little free acid and 0.5 g. of finely divided sulfur. After a short time, a little less than 2.38 g. of the alloy had

been disintegrated, the copper was precipitated as copper sulfide, and the solution was essentially free of copper. The copper sulfide contained some finely disseminated, undecomposed but still active alloy.

Example IX

A piece of alloy containing about 90% Ni, 3% Cu, 1.5% Al and 5.5% Si was heated in approximately 100 cc. of solution containing .85 g. Cu and 9.15 g. Ni both as chlorides and a few drops of concentrated HCl together with 0.7 g. of finely divided sulfur. The reaction causing precipitation of copper sulfide proceeded for a short time but then slowed down due to a coating of Si on the surface of the alloy. The addition of approximately 5 cc. of HF to the solution dissolved this coating so that the formation of the copper sulfide was again resumed. The reaction was not continued sufficiently long to remove all copper from the solution, but in a short time 1.07 g. of the alloy had been disintegrated and 0.98 g. of copper sulfide precipitate had been formed. There was some evolution of H_2S.

Example X

The initial solution contained 143 g. of Zn and 4.5 g. of Cu both as chlorides, 100 cc. of water and 40 cc. of 18° Bé. HCl. To this was added 27.2 g. of strip brass and 7.0 g. of sulfur. The whole was heated to boiling at which point the sulfur was melted and in the form of small droplets throughout the solution. After about 1 to 2 hours during which there was evolution of H_2S, 6.4 g. of the alloy had disintegrated with the precipitation of 10.5 g. of copper sulfide. The solution was copper free, the precipitate was essentially free of zinc and the remaining brass, while in this case having a thin surface film of copper enrichment, had a still reactive surface. Other experiments on brass indicate that the surface enrichment by copper is not always present.

Example XI

The initial solution of about 300 cc. contained 7.4 g. Cu, 12.8 g. Ni both as chlorides and 10 cc. concentrated HCl. To this was added 30.0 g. Monel metal and 10.0 g. of sulfur in pea size lumps. This was boiled for 2 to 3 hours and filtered. 14.0 g. of the Monel metal had been disintegrated with simultaneous precipitation of copper sulfide and some evolution of H_2S. The copper sulfide precipitate of 21.4 g. consisted of finely granular copper sulfide and some unreacted sulfur and contained a slight amount of flakes of Monel which, however, were still reactive. The solution was copper free, the surfaces of the residual scrap were essentially clean and were further reactive.

Example XII

An alloy containing 80% Cu and 20% Sn was heated in a solution consisting of 6.4 g. of Cu as Cu_2Cl_2 and 125.0 g. of Sn as $SnCl_2$, 100 cc. water and 20 cc. 18 Bé. HCl together with 5.0 g. finely divided sulfur. 7.6 g. of the alloy were disintegrated with the precipitation of copper sulfide. There were 18.9 g. of the copper sulfide residue which contained an excess of free sulfur. There was a slight generation of H_2S. The solution was copper free.

Example XIII

A copper tin alloy of same composition as Example XII (46.4 g.) was treated by heating in a solution of 50 cc. 18° Bé. HCl and 50 cc. water together with 3 g. of sulfur. After 1 or 2 hours during which there was some evolution of H_2S, 6.4 g. of the alloy had disintegrated forming 6.4 g. of copper sulfide precipitate and a copper free solution of stannous chloride. The precipitate contained essentially no tin and very little, if any, free sulfur.

Having thus described my invention, what I claim is:

1. A process comprising heating an aqueous acid solution containing an ion of the class consisting of chloride and sulfate in contact with elemental sulfur and a mixture in the metallic state including copper and a metal more electropositive than copper, whereby copper sulfide is formed and the more electropositive portion of said mixture is dissolved, and separating the resulting copper sulfide from the reaction mixture.

2. A process comprising treating an aqueous acid solution containing a salt of copper and a salt of a metal more electropositive than copper by heating said solution in contact with elemental sulfur and a mixture in the metallic state of copper with a metal electropositive to copper, whereby copper sulfide is formed and the metallic surfaces of said mixture remain substantially clean and reactive.

3. A process comprising treating an aqueous solution containing in solution a copper salt of the class consisting of sulfate and chloride and a salt of the class consisting of the sulfates and chlorides of a metal of the class consisting of aluminum, manganese, beryllium, zinc, iron, cadmium, cobalt, nickel, antimony and tin, by heating such solution in contact with elemental sulfur and a mixture including copper and another of said metals, whereby copper is precipitated as sulfide while the solution is enriched in said other metal.

4. A process comprising treating an aqueous acid solution containing copper and a salt of a metal more electropositive than copper by heating said solution in contact with elemental sulfur and an alloy of copper and a metal electropositive to copper, whereby the copper content of the solution is reduced and the metallic surfaces of the alloy remain substantially clean and reactive.

5. A process comprising treating a solution containing mixed chlorides of copper and nickel by heating the same in contact with elemental sulfur and a nickel-copper alloy in the metallic state.

6. A process comprising treating a solution containing mixed sulfates of copper and nickel by heating the same in contact with elemental sulfur and a nickel-copper alloy in the metallic state.

7. A process comprising treating a solution containing mixed sulfates of copper and cobalt by heating the same in contact with elemental sulfur and a cobalt-copper alloy in the metallic state.

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