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PROCESS FOR RECOVERING CERTAIN METALS OF THE THIRD PERIODIC GROUP

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This invention relates to an improved process for recovering certain known metals of the third periodic group and more particularly any known metal of said group having a melting point below 200° C.

In the periodic system of the elements now generally accepted the known metals of group 3, whose melting points are below 200° C., are indium and gallium, the melting points being about 155° C. and 30° C., respectively.

It is known that indium or gallium or indium and gallium are to be found associated with certain zinc ores, particularly the ore known as zinc blende. This ore contains the zinc principally in the form of zinc sulphide (ZnS).

To obtain the metallic zinc from such an ore it is the present practice to first roast the ore and then reduce it with finely divided coal in cylindrical fire-clay retorts, usually 4 to 5 feet long and about 8 to 10 inches in diameter, which are generally heated by gas. As the reduction of the oxide of zinc takes place at a temperature above the boiling point of the zinc, the vapor of the latter is led from the retort to a condenser made of fire-clay, where the volatilized metallic zinc is deposited in a molten state. At first a mixture of zinc oxide and metallic zinc in the form of a fine powder, known as zinc dust, is deposited. At a later stage the metallic zinc in liquid form is deposited. This is drawn off from the condenser from time to time and is cast into molds. This product is known as "spelter". It usually contains lead, as well as other metals, for example, cadmium and iron, as well as small quantities of arsenic, antimony and sulphur. In addition, there are quantities of the metals indium or gallium or both, where these metals exist in the ores.

In carrying out this distillation process the temperature of the retort contents is about that of the vaporization point of zinc, but after the principal portion of the zinc has passed to the condenser, the temperature in the retort rises, and the zinc which then passes off carries an appreciable proportion of lead. Therefore, it is the practice to run off the molten spelter from time to time and cast it into a series of molds. As a result, the bars of spelter vary in composition, those cast from the first runnings being more nearly pure zinc than those bars cast from the later runnings of a retort charge, the later cast bars being relatively high in lead.

Hence, under certain conditions it has been the practice at times to redistill the zinc material or at least that part of the zinc material which is high in lead, the second distillation process being so conducted as to distill off zinc, only, as nearly as possible, the distillation being terminated before any appreciable proportion of lead is driven off with the zinc. As a result of this manner of carrying out the redistillation of the spelter, there is left in the retort a residue relatively high in lead and hereinafter referred to as a leady residue of the redistillation of the zinc. I have discovered that this leady residue is especially high in indium or gallium or both indium and gallium, accordingly as those metals were present in the original ores, and this leady residue forms the starting material for that part of my process which comprises a series of steps for the recovery of the indium or of the gallium or of both from said leady residues, it being understood, of course, that the process as an entirety and broadly considered comprises the steps of obtaining the leady residue from the ores and then recovering from said leady residues the indium, or gallium, or both, contained therein.

The leady residue of the process of redistilling the zinc appears to consist largely of lead, and the indium, or gallium, or both, seem to be so held by the lead that it has not been commercially practical to recover either or both of them by any of the processes heretofore employed. Any attempts to dissolve out the indium or gallium or both by sulphuric acid, directly, will not be commercially satisfactory; apparently only a small part of the indium or gallium or both will be dissolved by the acid. It may be that this is due to the fact that the molecules of the indium, or gallium, or both, are so shut up in the lead that the latter forms a protective coating to prevent access of the sulphuric acid to the said indium or gallium or both.

In order to overcome the difficulty pointed

out above, I combine with the leady residue (the latter being in a molten condition) a material which can be dissolved by sulphuric acid and which will not interfere with the subsequent steps of the process. This added material is so combined with the molten leady residue, as for example by stirring, that it will be well distributed through the molten mass. It may be that as a result of this step the particles of lead are segregated from each other by the particles of the added material. Whether this is the true theory or not, the result is that after the treatment with sulphuric acid hereinafter more fully referred to, the lead is left in a finely subdivided condition, and it will be found that practically all the indium, or gallium, or both, present in the starting material, will be dissolved by the sulphuric acid.

While it is possible to employ various materials soluble in sulphuric acid for mixture with the molten leady residue, I have found that it is best to use for said purpose a metallic material which will melt at the temperature of the molten starting material, and which will not increase the number of steps of the subsequent treatment. Where the starting material contains only indium or gallium, but not both, then it is of advantage to add to the molten starting material either indium or gallium, respectively, but where the starting material contains both indium and gallium, then either indium or gallium may be added, but most advantageously indium. The added metal will be recovered readily together with the corresponding metal present in the starting material.

Instead of adding either indium or gallium to the molten starting material, I may add sufficient zinc to bring the total zinc content of the mixture to about 4% by weight of the total. This added zinc will be recovered together with the zinc existing in the starting material in the subsequent steps of the process.

However, any metal which will be precipitated from a sulphuric acid solution by hydrogen sulphide gas may be employed, because the treatment, with the gas, is an advantageous step in my process and, therefore, the addition of such a metal to the molten starting material does not increase the number of subsequent steps of the process.

While there are several metals which have this property of being precipitated by hydrogen sulphide gas, I have found that cadmium is particularly satisfactory for the purpose.

When the starting material contains indium and gallium, as is generally the case, I have found that greatest advantage is obtained by adding to the molten leady residue a small amount of metallic indium and thoroughly incorporating this with the molten residue as by a thorough stirring. Whether this metallic indium forms an alloy with the lead, or not, is immaterial. The fact is it readily accomplishes the desired result.

While the proportion of metallic indium to leady residue may be varied within considerable limits, I have found that it is not necessary to use more than about one part by weight of metallic indium to 20 parts of molten leady residue. When the indium has been thoroughly incorporated with the molten material, the latter may be then cooled and worked to shavings in a milling machine. However, I find it better to pour the molten material slowly, and most advantageously so as to fall drop by drop, into water. The temperature of the water is not highly important, though in practice it need not be heated. As the drops of molten material strike the water, the drops flatten out and are cooled to the solid state in the form of very thin scales, plates or laminæ. The resultant product is then dried.

The above-mentioned milling step, as well as this pouring step, is employed for the purpose of obtaining the solid material in a form exposing a large surface area to the action of the acid.

The product obtained by either of the methods described above is dried and then subjected to the action of sulphuric acid. In the best embodiment of the invention concentrated sulphuric acid is employed. The receptacle may be of such material as will not be acted upon by the acid, but must not be iron. In ordinary practice a receptacle of glass or porcelain is satisfactory. The comminuted or laminated metallic material is placed in the receptacle and concentrated sulphuric acid poured upon it. While a considerable variation in the proportion of acid to metal is permissible, it must be used in excess and in the usual practice it is well to employ about two parts by weight of concentrated sulphuric acid to one part of the said metallic material. Heat is then applied until the temperature rises to the point where acid fumes are evolved. Then the solution is maintained at this temperature until the lead has disintegrated to a finely divided condition, care being taken to continue the heating until no lumps remain. Usually this step of the process does not require more than 10 to 20 minutes. This step broadly considered consists in converting all the metals other than the lead into soluble sulphates. The resultant solution containing the finely divided lead is then allowed to cool to room temperature, after which water is added to it in suitable quantity to dilute the solution. In practice about one-half a liter of water is added for every 1000 gms. of the leady residue employed as the starting material. The whole mixture is then allowed to stand until all the lead has settled to the bottom. Then the supernatant liquid is decanted off. The

lead material remaining is washed with water on a filter once or twice, the filtrate being added to the decanted liquid. The amount of additional water used for this washing is such as will make the total water added to the acid solution amount to about 800 cc. for each 1000 gms. of the original leady residue used as a starting material.

The solution obtained up to this point of the process contains the sulphates of zinc and of indium or gallium, or both, as well as sulphates of some other metals which are usually associated with the ores. In the usual practice there may be and usually are found, in the said solution, salts of silver, germanium and bismuth. Also sometimes salts of thallium are present.

The next step of the process is to remove from the solution the metals other than zinc, indium or gallium. This may be done by passing hydrogen sulphide gas through the solution so long as a precipitate is formed. The solution is then filtered and the precipitates on the filter may be saved until enough are accumulated to justify treatment of said precipitates for the recovery of the germanium, whereupon the germanium may be recovered from said precipitates by any desired method.

The filtrate is allowed to stand for some time to allow the hydrogen sulfide to escape, or, to hasten this, the said filtrate may be subjected to an air blast to drive off any hydrogen sulphide gas which may have remained in the liquid. This liquid is a solution of sulphates of indium or gallium or both, according as either or both metals were in the starting material and, in any case, also contains some zinc sulphate.

This solution is now used as an electrolyte in order that the zinc and also indium, if the latter be present, may be thrown out or plated-out of the solution by a direct current. Usually a current of about 8 volts with a density of about 5 to 10 amperes per 100 square cms. of the cathode is required. The anode should be insoluble in the electrolyte and, hence, a platinum anode is advantageous. The cathode, however, while advantageously of platinum, may be of cheaper material, if desired. It has been found that a cathode of copper is satisfactory for practical purposes since the copper does not go into solution in the electrolyte, or at least not to an injurious extent.

In this step the bath should be maintained at a temperature of about 4.4 to 32.2° C., the purpose being to deposit the metal in a spongy condition on the cathode.

At the start of the plating process the metal deposited is zinc only, if no indium be present in the leady residue which served as a starting material, and under such circumstances the plating is continued until practically all the zinc is deposited from the electrolyte.

In most cases, however, the electrolyte contains indium. Under these circumstances, the zinc and indium deposit from the electrolyte onto the cathode, but at varying rates. At first the deposit is chiefly zinc, with, however, a small proportion of indium. Later when most of the zinc has been plated out of the electrolyte, the deposit will be mostly indium. Hence, to reduce the subsequent labor of separating the indium from the zinc, it is advantageous to remove the cathode when the indium deposit becomes apparent and replace it with a fresh clean cathode, so that the indium plated on the latter will be nearly pure. It is very advantageous to have this second cathode of indium. In practice, it will be found that in this way a deposit of indium about 99% pure may be obtained.

The deposited indium and zinc may be stripped from the cathode or cathodes and the stripped deposit then treated to recover the indium separate from the zinc.

A simple method of accomplishing this result is to subject the stripped coating to the action of hydrochloric acid, whereby the zinc is dissolved and the indium is left in a substantially pure metallic condition. The indium thus obtained may be remelted and cast into any desired form.

Where the electrolytic step is carried out with two cathodes used seriatim, as hereinbefore explained, the deposit on the second cathode is generally so nearly pure indium that it may be satisfactory for some commercial purposes to use the metal in this condition, thereby avoiding the necessity of further refining to remove the small amount of zinc present. Where there is no gallium present in the leady residue used as a starting material the process may terminate with the recovery of the indium.

Where, however, gallium is present, the acid liquor remaining after the zinc or zinc and indium have been plated out is then treated to render it alkaline. This may be done by adding a suitable alkaline material. Any indium which may not have been removed by the electrolytic process will be precipitated by the alkali, and may be filtered out. At this stage of the process, it is likely that the caustic soda converts both the indium sulphate and the gallium sulphate to hyroxides, which precipitate. The indium hydroxide remains as a precipitate, whereas the gallium hydroxide is quickly redissolved by the excess of caustic soda, perhaps by the formation of a chemical compound of gallium and soda.

In the best embodiment of the invention sufficient caustic alkali, for example, an aqueous solution of sodium hydroxide, is added to the acid bath to give a strong alkaline reaction when tested with methyl orange as an

indicator. In place of sodium hydroxide, potassium hydroxide may be used. The alkali should be in excess. The solution is filtered to free it from the precipitated indium, if there be any. This solution forms an alkaline bath which is used as an electrolyte with platinum electrodes, and with current strengths and densities such as described hereinbefore in connection with the removal of zinc or zinc and indium.

In practice I have found it advantageous to allow the temperature of the bath to rise as it may, because the gallium will deposit more rapidly from a warm bath than from a cold one. The gallium will collect on the cathode in drops and as these increase in size they will run down and drop off the cathode to the bottom of the tank or vat, where they may be caught in a suitable receptacle, such as a glass or porcelain vessel placed below the cathode. The gallium so collected is generally in so nearly a chemically pure condition that no refining steps are necessary. However, for extreme chemical purity, it may be refined by any of the usual methods. This completes the process for the recovery of gallium.

It will be noted that the process of recovering gallium includes all the steps necessary for the recovery of indium, if that be present in the starting materials, because it is necessary in carrying out the process for the recovery of gallium to include the step of subjecting the acid solution to electrolytic action, whether indium be present or not, in order to remove the zinc which is always present.

As one example of the manner of carrying out the process, the following is submitted:

The starting material, as hereinbefore stated, is a residue obtained from the redistillation of zinc, containing a considerable percentage of lead, with, of course, some zinc.

To 100 grams of this leady residue in a molten condition is added 5 grams of refined indium, which is thoroughly incorporated with the molten residue by continuous stirring while heating the material to maintain it molten. After about 5 minutes stirring, the molten material is poured slowly into water to allow the molten material to fall as individual drops which when they enter the water tend to flatten out as very thin leaves, or laminæ, so that they will expose as large a surface as possible to the action of acid in a subsequent step of the process.

The material is then removed from the water, drained and dried, the drying temperature being advantageously about 100° C., and usually not requiring more than 30 minutes for the quantity hereinbefore mentioned.

The next step comprises subjecting the dried material to the action of concentrated sulphuric acid. This acid is used in excess, it being best to employ 2 gms. concentrated sulphuric acid (of about 1.84 specific gravity) for every 1 gram of metallic material to be treated.

To subject the metal to the acid, it is best to employ a receptacle of glass or porcelain, first place the metallic material in it and then add the concentrated acid. The receptacle is then heated to and maintained at a temperature at which it will give off acid fumes for a period of 10–20 minutes, at the end of which time the lead which is present will be found to be disintegrated, so that it has the appearance of wet powdered lead.

As soon as the lead has been completely disintegrated to a finely divided condition as above described, the material is allowed to cool to room temperature. Then water is added in the proportion of about ½ liter to each kilogram of the original starting material. After thoroughly agitating the mixture, as by stirring, the whole is allowed to stand until all the lead has settled to the bottom. Then the supernatant liquid is decanted off. The decanted liquid contains, in solution, the sulphates of the metals indium and gallium which it is desired to recover. The lead powder may, if desired, be washed on the filter once or twice and the filtrate added to the above-mentioned supernatant liquid. The resulting solution should contain about 800 cc. of water for every 1000 grams of the original leady residue used as a starting material.

In practice it is found that the solution of the sulphate of indium and gallium also contains other salts in solution, for example, salts of zinc, silver, germanium and bismuth. The next step in the process is to remove from the solution the said salts of metals other than zinc, indium and gallium. This is done by passing hydrogen sulfide gas through the solution so long as a precipitate is formed.

Then the solution is filtered to remove the precipitates. The filtrate is then allowed to stand for some time to allow any excess of hydrogen sulfide gas in the solution to escape, or better still, the solution is agitated with an air blast to expel the excess of H_2S. The resultant liquid is a solution containing principally indium and gallium accompanied by some zinc.

The solution, which is acid, is now used as an electrolyte, being placed in a suitable container, and subjected to the action of a direct current. In doing this, an insoluble anode is used as, for example, platinum, and the cathode is preferably platinum, but satisfactory results are obtained by using copper. The electric current at about 8 volts is best used at a density of 5 to 10 amperes per 100 square cms. of the cathode. The bath should be kept at a temperature of about 40–90° F.

Within a few minutes after turning on

the current a deposit will appear on the cathode. This consists of zinc generally accompanied by some indium. As the zinc seems to plate out more rapidly than the indium, it is advisable after a few minutes to remove the cathode first employed and replace it by a new cathode, which will then be plated almost wholly by indium, practically all the zinc having been plated out from the electrolyte onto the cathode first employed. It is very advantageous to have this second cathode of metallic indium because the indium plated onto it will be nearly pure. After this electrolytic step has been carried on for about 8 hours practically all the indium will have been removed. Then the electrolyte is made alkaline with an aqueous solution of caustic soda, the latter being present in excess in the final solution. In practice, the caustic soda is present in the final solution to the extent of about 5% in excess. Any indium which may not have been removed by the preceding electrolytic treatment will precipitate out from the alkaline solution. The solution may then be filtered to remove the indium precipitate, which may be added to a subsequent bath of starting material, if desired.

The alkaline solution which contains, principally, salts of gallium, is used as an electrolyte, the anode being preferably insoluble, such as platinum, and the cathode either platinum or copper. The current strength and density may be as before stated for the deposit of indium. Practically all the gallium will be plated out of the electrolytic bath in about 4 hours.

The indium deposited on the first cathode used in the first electrolytic treatment may be separated from any zinc associated with it, by subjecting the material, stripped from the cathode, to the action of dilute hydrochloric acid, which will dissolve the zinc, but not the indium. The indium coating on the second cathode when stripped therefrom is usually of sufficient purity to be used commercially without further refining. Where the second cathode was of metallic indium, no stripping will be necessary.

What I claim is:

1. In a process of obtaining a metal of the third periodic group having a melting point below 200° C., from a starting material containing the said metal associated with lead, the steps which comprise melting said material, combining therewith a metal of the third periodic group such as is contained in the starting material, then comminuting the resultant product and subjecting it to the action of sulphuric acid to form a soluble sulphate of the said metal of the third periodic group.

2. In a process of obtaining indium and gallium, separately, from a starting material containing both, the steps which comprise melting said starting material, adding one of the said metals to the molten starting material, and eventually subjecting the mixture to the action of sulphuric acid to form soluble sulphates of said indium and gallium.

3. The process of separating and recovering indium and gallium, from material containing both elements, which comprises forming the sulphate salts of both elements, preparing an acid aqueous solution of said sulphate salts, electrolyzing the solution to deposit the indium, then adding alkali to the remaining solution to render it alkaline, and electrolyzing this alkaline solution to deposit the gallium.

4. The process of obtaining indium and gallium, which consists in intimately incorporating metallic indium with a molten leady residue of a zinc redistillation process, cooling the mixture, comminuting it, then subjecting it to the action of hot concentrated sulphuric acid to form soluble sulphates of indium and gallium, adding water to form an aqueous acid solution of said sulphates, freeing the solution from the lead, subjecting it to the action of hydrogen sulphide to remove any metals other than zinc, indium and gallium, electrolyzing the solution with two cathodes used seriatim, whereby first zinc and indium are deposited on one cathode and then nearly pure indium on the second cathode, then adding alkali in excess, filtering the solution and electrolyzing it to deposit the gallium.

In testimony whereof, I have hereunto set my hand.

FRANK G. McCUTCHEON.