Fig. 1

ELECTRODEPOSITION OF ARSENIC FROM ACID ELECTROLYTES

Inventor:
KENNETH L. LAWRENCE

Harold B. Croasdale
Hugh K. Spaulding

Attorney

 nickel sulphate crystals
Ni 30.0%
Cu 0.25%
Fe 1.0%
Zn 0.5%
H₂SO₄ 1.0%

black acid
H₂SO₄ 1200 g/L
Cu Ni As Ni
3.7 8.0 14.0 14.0
Density 39° Bé

sheets 1
ELECTRODEPOSITION OF ARSENIC FROM ACID ELECTROLYTES

Kenneth L. Lawrence, Metuchen, Harold B. Crossdale, Woodbridge, and Hugh K. Spaulding, Plainfield, N. J., assignors to American Smelting and Refining Company, New York, N. Y., a Corporation of New Jersey

Application March 27, 1953, Serial No. 344,935

2 Claims. (Cl. 204—108)

This invention relates to a process for the electrodeposition of arsenic from acid electrolytes. More particularly, it relates to the removal of arsenic from copper tankhouse electrolytes by electrodeposition from acid solution of the arsenic therefrom.

Broadly, the process comprehends establishing an acid electrolyte having more than about 4.5 grams per liter of dissolved arsenic and an acid concentration of about 550—800 grams per liter, and electrolyzing the so-established electrolyte to deposit arsenic at the cathode.

The process of the invention is based on the discovery that the rate of deposition is critically important in obtaining efficient deposition of arsenic during electrolysis of acid electrolytes having arsenic dissolved therein; and that the maximum rate of deposition per ampere-hour can be obtained with electrolytes containing acid in the range of about 550—800 grams per liter and having more than about 4.5 grams per liter of arsenic dissolved therein.

The invention is particularly useful in removing arsenic from tankhouse electrolytes used in the electrolytic refining of copper. In such copper refining, impure copper anodes containing arsenic, along with other impurities, are electrolyzed in a suitable bath of acid electrolyte which in commercial operations is an aqueous solution of sulfuric acid and copper sulfate. During the electrolysis the copper in the anode passes into solution in the acid electrolyte and is deposited thereon from the tankhouse as substantially pure copper. Impurities associated with the copper in the anode, including arsenic, are partly dissolved in the electrolyte and in part are thrown down as anode slimes. Other impurities are substantially entirely thrown down in these slimes.

Because the copper anodes continuously supply dissolved arsenic to the electrolyte, this and other impurities gradually accumulate therein and it becomes necessary either periodically or continuously to remove large quantities of the tankhouse electrolyte in order to maintain the requisite purity of the electrolytic bath. Such removed electrolyte is treated in accordance with the present process to remove arsenic therefrom, after which the electrolyte may be further treated in any suitable manner to remove other impurities, and the purified electrolyte returned to the tankhouse.

Thus, in a narrower aspect of the invention, there is established from the electrolyte removed from the tankhouse an electrolyte having about 550—800 grams per liter of sulfuric acid and having a dissolved arsenic content greater than about 4.5 grams per liter. For best results, the electrolyte also preferably contains dissolved copper not in excess of about 0.9 gram per liter. Such electrolyte is then subjected to electrolysis with deposition of the arsenic at the cathode until the dissolved arsenic is reduced to an amount not below about 4.5 grams per liter. Thereafter, the electrolyte, preferably after it has been further treated to remove or reduce other impurities therein, may be returned to the tankhouse.

Any soluble or insoluble electrodes, includes arsenic or arsenic-containing electrodes, may be used in the process. For best results, when practicing the process to remove dissolved arsenic from solution and especially from tankhouse electrolytes, the electrodes are insoluble anodes such as, for example, lead or carbon anodes, and the cathodes are metallic cathodes, preferably copper cathodes.

The voltage across the electrodes in the electrolytic cell during the electrolysis may be considered to be self-adjusting and has been found to assume a value in the range of about 1.50—2.65 volts. Any desired amperage and current density may be used. In conducting the process on a plant-scale, current densities of 10—20 amperes per square foot have been used and these are the preferred current densities for the process. Temperature of the electrolyte appears to have no particular effect upon the electrolysis. Electrolytic temperatures up to about 130° F. may be used advantageously. However, temperatures in the range of about 80 to 130° F. are preferred.

The invention is further illustrated in the accompanying drawings and examples. It should be understood, however, that the drawings and the examples are given for purposes of illustration and that the invention in its broader aspects is not limited thereto.

In the drawings:

Fig. 1 is a flowsheet illustrating use of the process of the invention to remove arsenic from copper tankhouse electrolytes.

Fig. 2 illustrates arsenic removal from acid arsenical electrolytes and is a curve in which arsenic removal in terms of grams per ampere hour is plotted against acid concentration in terms of grams per liter.

Referring now to the flowsheet of Fig. 1, impure copper anodes cast from an anode furnace and containing arsenic together with other impurities, are placed in a sulfuric acid-copper sulfate electrolyte in the tankhouse electrolytic cells, illustrated by numeral 1. Upon passing current from the anode to the cathode, the copper in the anode dissolves in the electrolyte and is deposited as high purity copper on the cathode during the electrolysis. The impure copper anodes also contain some oxides of copper which chemically dissolve in the electrolyte and increase its copper content. The tankhouse electrolysis, however, proceeds most efficiently when it has a copper concentration of about 40 grams per liter. The excess copper which tends to build up in the tankhouse electrolyte due to the solution of the copper oxides, may be removed in A section cells illustrated by the numeral 2 in the drawing. This may be accomplished by recycling a portion of the tankhouse solution through the A section cells where the recycled liquor is electrolyzed, using an insoluble anode. The copper removed in the cathodes in the A section cells is high grade commercial copper.

Unless removed from the electrolyte, the impurities in the tankhouse anodes which are dissolved or only partially dissolved during the electrolysis (arsenic being included in this latter group) concentrate in the tankhouse electrolyte until they interfere with the purity of the deposited copper at the cathode. The undissolved impurities in the anodes collect in the bottom of the cells at the anode and are referred to in the art as anode slimes or muds. The regeneration of the electrolyte from the cells 1 by the removal of arsenic and the removal of other impurities in the electrolyte together with an effective separation of the arsenic from the other impurities and the copper during the regeneration may be accomplished as follows.

The concentration of the dissolved copper in the cells 1, because of the electrolysis, tends to be high in the lower portion of the cells while the concentration of other dissolved matter in the electrolyte remains uniform throughout the cells. Advantage may be taken of this fact by use of the so-called Pyne-Green cells 3 which permit continuous partial withdrawal of part of the electrolyte from the top of the electrolyte in the tankhouse cells 1, thereby effecting a small but nevertheless less appreciable separation of the arsenic and other impurities from the copper. A portion of the electrolyte from the cells 3 having
a typical analysis as indicated in Fig. 1, is withdrawn from these cells, preferably as a continuous stream, and may be sent to the P section cells indicated by numeral 4. In the cells 4, this withdrawn solution may be electrolyzed with an insoluble lead anode and a copper cathode to remove a major portion of the dissolved copper. Preferably, this electrolysis is continued until the copper concentration is reduced to a value at which the copper cathodes upon continued electrolysis would become too soft, due to arsenic deposition, to be handled conveniently. Such copper cathodes from the F section cells being too impure for commercial copper, may be advantageously returned to the anode furnace for recasting for use as anodes in the copper tankhouse cells 1. It has been found that when the copper concentration in the F section cells has been reduced in the preferred amount, crystallization of copper sulfate and other impurities does not take place or does not take place in any appreciable amount when the residual electrolyte from the F cells is subsequently concentrated by evaporation to an acid concentration of about 550–800 grams per liter. It has been found, further, that when the copper concentration has thus been reduced to about 9 grams per liter, such crystallization and softness of the cathodes does not occur.

The electrolyte from the F section cells 4, having a typical analysis indicated in Fig. 1, is passed to an evaporator or evaporators 5 where the solution is concentrated by evaporation until its acid content is increased to about 550–800 grams per liter H₂SO₄, the preferred value in this range being about 600 grams per liter. The thus concentrated solution contains more than about 4.5 grams per liter of dissolved arsenic and in the course of experimentation with this process on a plant-size scale over a period of several months it was found to contain not less than about 8 grams per liter of dissolved arsenic. A typical analysis of the electrolyte from the evaporator 5 is indicated in the drawing.

The electrolyte from evaporator 5 is passed to the P section cells indicated by the numeral 6 where the solution is further electrolyzed to deposit arsenic at the cathode, the electrolysis being conducted with high current efficiency until the arsenic concentration has been reduced to a value not below about 4.5 grams per liter. As indicated by the typical analysis of the solution from the P section cells shown in the drawing, the electrolysis in these cells is continued until the arsenic concentration has been reduced to a value of about 4.5 grams per liter.

Any suitable electrodes may be used in the P section cells. The voltage of the cells is self-regulating and any desired amperage and current density may be used. In the plant-size experimentation referred to, lead anodes and copper cathodes were used. The voltage on the cells was found to be in the range of about 1.8–2.65 volts. 5000–6000 amperes were used in the cells at a current density in the range of 10–20 amperes per square foot. It was found that during this electrolysis arsenic removal was slight until the copper was reduced to a value below about 0.9 gram per liter. The arsenic which was deposited at the cathode did not, for the most part, adhere to the cathodes but collected as a sludge at the bottom of the cell in the vicinity of the cathodes. A typical analysis of the cathode sludge is illustrated in the drawing. It was found, unless kept wet, this sludge has a strong tendency to burn spontaneously when exposed to air with the evolution of fumes of oxides of arsenic.

The sludge collected in the P section cells may, if desired, be further treated to recover valuable constituents therein. Thus, it may be washed to remove the nickel and acid therein, after which it may be burned to separate the arsenic from the copper. During the burning, the arsenic is converted to fumes of oxides of arsenic which may be cooled and collected in a baghouse. The residual copper, which is in the form of copper mixed with oxides of copper, may be used as such or further refined to pure copper.

The residual electrolyte from the P section cells may be passed to a suitable crystallizer 7, such as an iron pan crystallizer, where it may be further concentrated and cooled to precipitate nickel sulfate crystals which may have the typical analysis indicated.

The so-called black acid, which is the mother liquor from the crystallizer 7 and having the typical analysis indicated, may be used in any suitable manner for its acid values. It has been found, however, that its arsenic content and the content of the other impurities are sufficiently low so that it may be used in the tankhouse without affecting either the efficiency of the deposition or the purity of the copper deposited at the cathodes therein. Preferably, the mother liquor is recycled to the cells 1.

Alternately, instead of using the F section cells 4, the withdrawn tankhouse electrolyte may be passed either from the cells 3 or the cells 1 directly to the evaporator 5 and concentrated therein. In such event, copper sulfate, which may also contain nickel sulfate, may crystallize in the evaporator and may be recovered for use elsewhere. Alternatively also, the residual electrolyte from the P section cells may be returned to the tankhouse for use therein. Preferably, however, such electrolyte from the P section cells is further treated in the crystallizer 7 in the above discussed manner before it is used in the tankhouse.

The invention is further illustrated in the accompanying examples, in all of which lead anodes and copper cathodes were used.

**EXAMPLE I**

A series of arsenical electrolytes having varying concentrations of sulfuric acid were made up from black acid of the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>1100</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1</td>
</tr>
<tr>
<td>As</td>
<td>0.4</td>
</tr>
<tr>
<td>Sb</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The test solutions were electrolyzed under the conditions noted and with the results set forth in table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Test Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. ° F</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>81</td>
<td>125</td>
<td>120</td>
</tr>
<tr>
<td>H₂SO₄ g/lt.</td>
<td>350</td>
<td>500</td>
<td>550</td>
<td>600</td>
<td>650</td>
<td>700</td>
<td>750</td>
</tr>
<tr>
<td>As, g/lt.</td>
<td>16.2</td>
<td>21.4</td>
<td>27.0</td>
<td>32.5</td>
<td>37.8</td>
<td>27.0</td>
<td>32.5</td>
</tr>
<tr>
<td>Cu, g/lt.</td>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
<td>0.10</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>Ni, g/lt.</td>
<td>1.1</td>
<td>1.5</td>
<td>1.8</td>
<td>2.2</td>
<td>2.6</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Pb, g/lt.</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Volts</td>
<td>2.80–2.85</td>
<td>2.55–2.65</td>
<td>2.55–2.65</td>
<td>2.55–2.69</td>
<td>2.55–2.69</td>
<td>2.57</td>
<td>2.65</td>
</tr>
<tr>
<td>Test Duration, Minutes</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>35</td>
<td>35</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>As Removed, Grams per</td>
<td>0.114</td>
<td>0.136</td>
<td>0.220</td>
<td>0.220</td>
<td>0.220</td>
<td>0.118</td>
<td>0.211</td>
</tr>
<tr>
<td>Amp, Hour</td>
<td>0.245</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results obtained are plotted in the curve of Fig. 2, in which arsenic removal per ampere-hour is the ordinate and acid concentration in grams per liter is the abscissa. It will be noted that maximum current efficiency occurs with acid concentrations in the range of about 550–800 grams per liter.

**EXAMPLE II**

An arsenical electrolyte having the analysis shown in Table 2 was prepared and electrolyzed, using a current of 4.6 amperes in the test cell. Arsenic removal as given in the table was obtained.

<table>
<thead>
<tr>
<th>Time, Hours</th>
<th>H₂SO₄ g/l.</th>
<th>As g/l.</th>
<th>Cu g/l.</th>
<th>Ni g/l.</th>
<th>Arsenic Removed g/l.</th>
<th>Grams per Amp-Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>569</td>
<td>22.2</td>
<td>25.0</td>
<td>18.0</td>
<td>15.5</td>
<td>0.23</td>
</tr>
<tr>
<td>2.0</td>
<td>569</td>
<td>22.2</td>
<td>25.0</td>
<td>18.0</td>
<td>15.5</td>
<td>0.23</td>
</tr>
</tbody>
</table>

It will be noted that high copper and nickel concentrations in the electrolyte do not affect the current efficiency with which the arsenic is removed.

**EXAMPLE III**

An arsenical electrolyte having the analysis shown in Table 3 was electrolyzed, using a current of 4.6 amperes in the test cell. The results given in this table were obtained.

<table>
<thead>
<tr>
<th>Time, Hours</th>
<th>H₂SO₄ g/l.</th>
<th>As g/l.</th>
<th>Cu g/l.</th>
<th>Ni g/l.</th>
<th>Arsenic Removed g/l.</th>
<th>Grams per Amp-Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>645</td>
<td>7.4</td>
<td>4.2</td>
<td>12.6</td>
<td>2.0</td>
<td>0.23</td>
</tr>
<tr>
<td>2.0</td>
<td>645</td>
<td>7.4</td>
<td>4.2</td>
<td>12.6</td>
<td>2.0</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Arsenic removal was slight until the dissolved copper concentration had been reduced to a value not in excess of 0.9 gram per liter. It will be noted that the arsenic is removed with high current efficiency until the dissolved arsenic concentration is reduced to a value below about 4.5 grams per liter.

From the foregoing, it will be seen that the present invention affords a method for the electrodeposition of arsenic from acid-arsenic electrolyte at high current efficiencies. Although the efficiencies described herein are obtained with any acid electrolyte, the process is most useful in connection with mineral acid electrolytes, and particularly sulfuric acid electrolytes of this type.

What is claimed is:

1. In the removal of arsenic from a sulfuric acid copper tankhouse electrolyte having a dissolved arsenic content such that the electrolyte is concentrated by evaporation to an acid content of at least about 550 grams per liter the electrolyte will contain more than about 4.5 grams per liter of dissolved arsenic, by a process involving removal of copper and arsenic by electrolysis in separate steps, the improvement comprising subjecting the tankhouse electrolyte to electrolysis with an insoluble anode to remove copper from the electrolyte, discontinuing said electrolysis before the resulting cathode becomes too soft for handling, thereafter concentrating the residual electrolyte by evaporation until its acid content is in the range of about 550–800 grams per liter, and electrolyzing the concentrated electrolyte in said acid range with an insoluble anode until the arsenic content is reduced to an amount not below about 4.5 grams per liter.

2. A process for treating a sulfuric acid copper tankhouse electrolyte having nickel and arsenic dissolved therein, the arsenic being present in an amount such that when the electrolyte is concentrated by evaporation to an acid content of at least about 550 grams per liter the electrolyte will contain more than about 4.5 grams per liter of dissolved arsenic comprising: electrolyzing said tankhouse electrolyte with an insoluble anode until the dissolved copper content is reduced to about 9 grams per liter, thereafter concentrating the residual electrolyte by evaporation until its acid content is in the range of about 550–800 grams per liter, and then electrolyzing the concentrated electrolyte in said acid range with an insoluble anode until the arsenic content is reduced to an amount not below about 4.5 grams per liter, crystallizing nickel sulfate from said last mentioned electrolyte by further evaporating and then cooling the said mentioned electrolyte, and returning the resulting mother liquor to the tankhouse electrolyte.

References Cited in the file of this patent

**UNITED STATES PATENTS**

991,685 Aldrich et al. May 9, 1911

1,148,522 Martin Aug. 3, 1915

**OTHER REFERENCES**