

Denitrification of Chuquicamata Copper Solutions

Thesis by  
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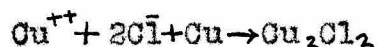
At Chuquicamata, Chile is located one of the world's largest copper mines. The ore is Brochantite, and carries an average of 1.8% copper, mainly as  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$ . The ore is crushed and leached with spent electrolyte, which comes from electrolytic tanks. The strong solution (i.e. solution strong in copper) from the leaching vats is dechloridized with cement copper and sent to the electrolytic tanks where the copper is removed by passing electricity thru the solution by means of insoluble lead-antimony anodes. The spent electrolyte, which contains a fair amount of free sulphuric acid, is sent back to the leaching vats. The copper cathodes are later melted and cast.

Thus it is seen that the process is a cyclical one. It is not necessary to add sulphuric acid during the leaching; in fact, during each cycle, an amount of sulphuric acid is gained which is equivalent to the copper sulphate content of the ore. Hence, during each cycle, a certain amount of spent electrolyte is replaced by water, and, in this way, various other salts which occur in the ore are kept from accumulating in the solutions.

Of the impurities, the least desirable are chloride, ferric, molybdate and nitrate ions. Chlorides are decomposed into chlorine in the electrolytic tank thus lowering the current efficiency, and, moreover, are deposited upon the cathode as cuprous chloride, which, during the subsequent melting of the cathodes, volatilizes, resulting in a copper loss. Ferric ion lowers the current efficiency by becoming reduced at the cathode, migrating over to the anode, and then being oxidized. Molybdate ion tends to catalyze the reaction between ferrous ion and nitric acid, thus oxidizing the iron and hence lowering the current efficiency. Because of its ability to exist in two valence states it also may act similar to the iron.

Nitric acid, especially in the presence of nitric oxide, attacks lead readily at the anode. By constructing the anodes of an alloy containing 50% lead and 50% antimony, this effect is greatly diminished, but the anodes have the disadvantage of being both brittle and costly. By discarding portions of the spent electrolyte, as was mentioned above, other ions in solution, namely  $As^{+++}$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{++}$  and  $Al^{+++}$ , can be maintained at concentrations which are not harmful.

Chloride ion has in the past been removed by passing the solution over a copper surface, which precipitates cuprous chloride according to the reaction:



By this means the chloride ion concentration can be decreased to 0.2 g/l.

Recently, a method known as "The Limerock Process" has been developed on a semi-commercial scale at Chuquicamata in order to partially remove molybdenum and iron from the strong solution (i.e. the solution from the leaching vats). In order that this process be economically feasible it was necessary to develop a different method of leaching in order to obtain strong solutions which carried a small percent of free sulphuric acid. In the past a system known as the normal leach was carried out which developed a strong solution carrying 40 g/l of copper and 35 g/l of acid, from a spent electrolyte carrying 15 g/l of copper and 70 g/l of acid. The new counter current leach, using the same spent electrolyte, develops a strong solution carrying 60 g/l of copper and 8 g/l of acid. In the latter solution, all of the other elements remain in the same concentration except molybdenum, which builds

up to three times the concentration of that element in the normal leach solutions.

The counter current strong solution is treated with potassium chlorate to oxidize all of the iron and then with limerock until an amount has been added which will just precipitate  $\text{Fe}(\text{OH})_3$  but not yet  $\text{CuCO}_3$ . This end point is determined by noting when a brown ring of ferric hydroxide forms on a filter paper thru which 5c.c. of the solution has passed. At this time, gypsum is added for a filter aid, and the precipitates of  $\text{Fe}(\text{OH})_3$ ,  $\text{Mo}(\text{CO}_3)_3$  and  $\text{CaSO}_4$  is filtered, washed and discarded. The excess wash is stripped of its copper by adding an excess of limerock and filtering off the basic carbonate precipitate of copper with an Oliver filter; the filtrate is discarded. This precipitate is later added to the counter current strong solution just before adding the first limerock.

The filtrate from the iron and molybdenum precipitation is sent to a blending tank where it is mixed with strong solution from the normal leach; the total solution is dechloridized and sent to the electrolytic tanks. The spent electrolyte is recirculated, in accordance with the need, to each of the two leaching vats. The normal leach handles  $62\frac{1}{2}\%$  of the total ore while the counter current leach handles the remainder.

Thus far, no system has been developed at Chuquicamata for the removal of nitric acid from solution. Since, in the counter current leach, it is necessary to oxidize ferrous iron with limerock in order to precipitate ferric hydroxide, it was suggested that it would be most economical to denitrify the counter current strong solution by causing the ferrous ion present to reduce the nitric acid to nitric oxide, perhaps by means of some catalyst, and thus

partially denitrify the solution and oxidize the iron at the same time, thus saving the expense of oxidizing the solution with a costly salt such as potassium chlorate. Since not enough ferrous ion is present to completely denitrify the solution, it was suggested that the ferric ion, resulting from the first reduction of nitric acid, might be reduced with copper and again<sup>bc</sup> allowed to further denitrify the solution. This process might be repeated until all of the nitric acid had been removed. If it were not possible to denitrify this strong solution, it was recommended that attempts be made to denitrify either the spent electrolyte or the normal strong solution and thus remove nitric acid from the system as a whole.

Five thousand pounds of ore, in thirty six sacks, were shipped from the mine to the California Institute of Technology. Nine sacks contained high nitrate ore, nine others high molybdenum ore, and the remaining eighteen contained regular ore. Analysis of copper, chloride, nitrate, and molybdenum were submitted with the shipment. Final results ought to be obtained from solutions actually derived from the ore by leaching, although preliminary experiments might be made upon synthetic solutions resembling actual Chuquicamata solutions and made up as follows:

(See page 5)

Grams per liter	Counter Current Strong Solution	Normal Strong Solution	Spent Electrolyte
Cu as $\text{CuSO}_4$	60	40	15
$\text{H}_2\text{SO}_4$	8	35	70
Fe as $\text{FeSO}_4$	1.5	1.5	1.5
As as $\text{As}_2\text{O}_3$	0.2	0.2	0.2
Al as $\text{Al}_2(\text{SO}_4)_3$	2.0	2.0	2.0
Mg as $\text{MgSO}_4$	0.5	0.5	0.5
Na as $\text{Na}_2\text{SO}_4$ , NaCl, & $\text{NaNO}_3$	11.0	11.0	11.0
K as $\text{K}_2\text{SO}_4$	2.5	2.5	2.5
Cl as NaCl	0.4	0.4	0.2
$\text{HNO}_3$ as $\text{NaNO}_3$	4.0	4.0	4.0
Mo as $\text{MoO}_3$	0.5	0.15	0.15

In studying the reaction between nitric acid and ferrous iron, and also other reactions appearing later in this paper, a solution (designated hence as the test solution) was made up which contained 4.0 g/l of nitrate, 1.5 g/l of ferrous iron and 70 g/l of sulphuric acid. It is to be noted that this solution contains those salts of the spent electrolyte which are active in the above reaction.

Except for the actual leaching solutions, all reagents and synthetic solutions were made from C.P. chemicals, using distilled water as the solvent. The quantitative system of analysis used was that adopted at the plant. Because of the great number of analyses to be run, no effort was made to attain better than 1% accuracy.

Ferrous iron was determined by titration in a sulphuric acid solution with standard potassium permanganate solution. Small errors often occurred due to reduced molybdenum and arsenic. Nitric acid

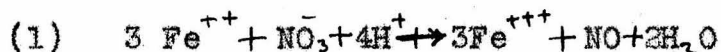
was determined by introducing the sample, after just oxidizing it with potassium permanganate, into 25 c.c. of concentrated sulphuric acid and titrating with a sulphuric acid solution of ferrous sulphate, the end point being taken when the characteristic brown color of the  $\text{FeNO}^{++}$  complex is noted. Sulphuric acid was determined by titrating the sample, after dilution with water, with standard sodium carbonate solution, using methyl orange as an indicator. The well known iodide method was used in analyzing for copper, after making a few alterations. The sample is first oxidized with hydrogen peroxide, evaporated to dryness to expel nitric acid, redissolved in water, neutralized with sodium carbonate and acidified with acetic acid; sodium fluoride is added to repress the ionization of iron. Potassium iodide is then added and the iodine liberated is titrated with sodium Thiosulphate standard solution in the usual way. For determining chloride, the Volhard method was used, except that the silver chloride precipitate was first filtered out of solution before titrating with standard ammonium thiocyanate; this alteration was necessary in order to obtain a permanent end point. No effort was made to analyze for other constituents.

During the greater part of the time, experiments were made in order to study the reaction of nitric acid and ferrous iron in dilute sulphuric acid solution. Solutions of from five to ten milliliters in volume were introduced into test tubes and these in turn were immersed in a constant temperature water bath which could be maintained at any temperature between thirty and eighty degrees centigrade, with a fluctuation in temperature of less than one half degree. The bath could accommodate fifteen test tubes. More than two thousand separate tests were made, varying in each case the conditions affecting the

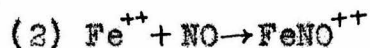
reaction (i.e. catalysts, acid concentration, temperature, salts, etc.)

#### Reaction of Nitric Acid with Ferrous Iron

The reaction studied is represented by the following equation:



The following mechanism tends to hold nitric oxide in solution:



This  $\text{FeNO}^{++}$  complex is easily broken up on passing air thru the solution; and moreover, when the partial pressure of nitric oxide is lowered sufficiently, it diffuses out of solution and the complex slowly spontaneously decomposes. In studying the rate of reaction (1), the time was noted for the first appearance of a brown color (the  $\text{FeNO}^{++}$  complex) and also for its final disappearance when all of the ferrous iron had been oxidized to the ferric state.

#### ACCELERATING FACTORS:

The reaction was found to be accelerated by:

- (1) An increase in temperature,
- (2) An increase in hydrogen ion concentration,
- (3) An increase in the concentration of both  $\text{Fe}^{++}$  &  $\text{NO}_3^-$ ,
- (4) An Increase in the weight ratio of  $\text{NO}_3^-$  to  $\text{Fe}^{++}$ ,
- (5) Various catalysts,

#### CATALYSTS:

Of the catalysts, the best was found to be nitric oxide, one of the reaction products; hence the reaction is autocatalyzed. The rate of reaction increases as the concentration of nitric oxide is increased. Silica gel was found to be the best of the insoluble



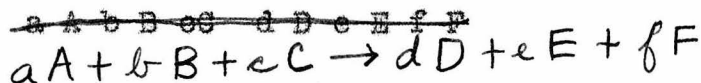
catalysts, no doubt due to its ability to adsorb large quantities of nitric oxide upon its surface and retain it even after washing. Hence the reaction readily takes place upon its surface due to the high concentration of the true catalyst, nitric oxide, which exists there. The action of the gel is accelerated if, before use, it is saturated with nitric oxide; it improves in use when in contact with solutions containing this gas. However on continued washing or drying, it loses much of its power as a catalyst, due perhaps to the removal of nitric oxide, but it can be revived by contact with the gas. Porous plate, crushed quartz, and diatomaceous earth behave similarly to the gel but much less effectively, due no doubt to their smaller surface of contact. Molybdate ion somewhat accelerates the initial formation of nitric oxide in an unfouled solution (i.e. a solution devoid of nitric oxide), especially upon long standing, but it tends to retard the completion of the reaction. Solutions, if they contain this ion, tend to foul within a short time due to nitric decomposition. Ferric ion also slightly catalyzes the reaction.

RETARDING FACTORS; THE SALT EFFECT:

Chloride ion seriously retards reaction (1) (by 50% even in small concentrations of 0.2 g/l), probably because of a complex compound which this ion forms with nitric oxide, thus diminishing the activity of the later.

In accordance with the Brönstead theory of the salt effect it might be expected from the nature of the reacting ions that the addition of soluble salts to the solution would retard the rate of reaction.

For a reaction:



the Brönstead theory gives the following expression for the rate of reaction (R):

$$R = K(A)^a (B)^b (C)^c 10^{-2\beta(Z_A Z_B + Z_A Z_C + Z_B Z_C) \sqrt{\Sigma c Z^2}}$$

where A, B, and C, are concentrations of the reacting ions, Z is the valence charge on the ion, c is the concentration of an added salt, and K and  $\beta$  are constants. The rate for equation (1) hence becomes:

$$R = K(Fe^{++})^3 (NO_3^-) (H^+)^6 10^{-2\beta(-2+2-1) \sqrt{\Sigma c Z^2}}$$

OR

$$R = K(Fe^{++})^3 (NO_3^-) (H^+)^6 10^{-2\beta \sqrt{\Sigma c Z^2}}$$

Hence as the ionic strength,  $\Sigma cz^2$ , of the solution increases, the rate, R, decreases; the effect is greater if the valence of the added ion is high. This was found to be true. Except for the reacting ions, all added salts retard the reaction and the order of their effect was as follows: (1)  $Cl^-$ , (2)  $Mo^{6+}$ , (3)  $Al^{+++}$ , (4)  $As_2O_3^-$ , (5)  $Cu^{++}$ , (6)  $Mg^{++}$ , (7)  $K^+$ , (8)  $Na^+$ , (9)  $NH_4^+$ . Chloride ion no doubt exerts some other marked influence upon the reaction. Ferrous Iron, contrary to expectations, in small quantities (2 g/l) catalyzes the reaction.

Stirring the solution accelerates the initial formation of Nitric Oxide as it established better contact with the solid catalyst. However, once sufficient nitric oxide has been formed to cause the reaction to occur rapidly, stirring the solution will retard the rate of reaction because this procedure assists the escape of the catalyst, nitric oxide, and hence lowers its concentration in solution. Passing air thru the solution has the same effect.

DATA CONCERNING REACTION (1):

The following table serves to illustrate the effect of concentration, temperature, catalysts, and dissolved salts upon the rate of

reaction (1):

Solution	Temperature	Catalyst	Time of reaction
1.5 g/l $\text{Fe}^{++}$ 4.0 g/l $\text{NO}_3^-$ 160 g/l $\text{H}_2\text{SO}_4$	45° C.	None	25 Hrs.
	45°	Silica gel	18 Hrs.
	45°	Silica gel treated with Nitric Oxide	3 Hrs.
	45°	0.4 g/l $\text{NO}_2^-$	25 Min.
	60°	0.4 g/l $\text{NO}_2^-$	3 Min.
As above, but 70 g/l $\text{H}_2\text{SO}_4$	60°	0.4 g/l $\text{NO}_2^-$	8 Min.
Spent Electrolyte	60°	0.4 g/l $\text{NO}_2^-$	20 Min.

CHARACTERISTICS OF REACTION (1):

A febrile reaction is one which is autocatalyzed. It occurs in three stages: (1) an incubation period, when the concentration of the catalyst is slowly being built up; (2) an induction period, during which enough catalyst has been formed to cause the reaction to occur rapidly; (3) a period of extinction, during which the rate gradually decreases, due to a deficiency of reagents.

Reaction (1) passes thru all stages but the third, in the case where the reagent in excess is nitric acid. During the first period, nitric oxide is slowly formed, but it is held in complex formation by ferrous iron (see reaction (2)), and its power as a catalyst is thus reduced. Hence the first period is very long, When nitric oxide, in excess of that held by the complex, has been formed, the reaction suddenly increases in rate. Additional nitric oxide hence appears from two sources at once, first, from the decomposition of nitric acid, and second from the complex which must give up its nitric

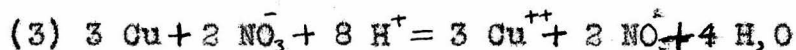
oxide because of the oxidation of ferrous iron. This additional gas immediately increases the rate. Thus, within a few seconds, the greater part of the reaction occurs at a surprisingly fast rate which increases as the ferrous iron concentration decreases. The slight catalytic effect of ferric iron also may be a factor increasing the rate. From this discussion it is obvious why a low nitrate to ferrous ion ratio decreases the rate.

REACTION (1) AS APPLIED TO CHUQUICAMATA SOLUTIONS:

In the light of the preceding results one sees that, except for the test solution, the most favorable solution for denitrification is the spent electrolyte, as it runs highest in acid and lowest in total salts. Reaction (1) is complete in three hours at 60°C. in the spent electrolyte in the presence of silica gel as a catalyst. However by introducing nitric oxide, in the form of nitrite ion, into the solution, the incubation period is eliminated and one may dispense with the gel. In this case the above reaction occurs in twenty minutes instead of three hours. At 75°C this time may be halved.

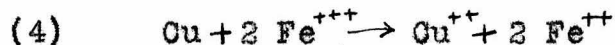
Since the spent electrolyte contains 4.0 g/l of nitrate ion and 1.5 g/l of ferrous iron, it is seen that with a complete oxidation of the iron only 0.55 g/l of nitrate are removed. Hence, once the reaction has occurred, it becomes necessary to again reduce the iron in order to remove more nitrate. Copper was found to be the best available reducing agent, but it was found that this metal could be used for reducing nitric acid directly rather than thru the intermediary, ferrous ion. This lead to another phase of the denitrification problem which will be treated below.

## Reaction of Copper in the Denitrification Process



The reaction of copper with nitric acid, like reaction (1), also is autocatalyzed by nitric oxide. Like a true febrile reaction, it goes thru all of the three periods mentioned before. For this reaction, the Brönstead theory predicts a negative salt effect as in the case of reaction (1), and this has been found to be the case. In all other respects ( i.e. influence of temperature., acid, etc.), it is similar to reaction (1).

Unfortunately, when copper is introduced into the solution, the following reaction also occurs:



This reaction appears to be but slightly affected by hydrogen ion or the presence of nitric oxide. Its rate increases slightly with temperature and is proportional to the surface of copper in contact with the solution. By constantly reforming ferrous ion, reaction (4) tends to retard both reactions (1) and (3). In general, reaction (3) will not progress until practically all of the iron is in the oxidized state. Hence, the problem is to adjust conditions so that reactions (3) and (1) will occur more readily than reaction (4).

Before copper is introduced, reaction (1) is caused to take place by passing nitric oxide into the solution and placing it in contact with silica gel. When all of the iron is in the ferric form, copper is placed in contact with the solution and it at once begins to dissolve, thus decomposing the nitric acid present. When the nitrate concentration has fallen to a low value, reaction (3) decreases in rate. However reaction (4) continues undiminished in speed, and

soon forms an appreciable amount of ferrous ion, which eventually completely stops all further denitrification despite the large amount of nitric oxide then present. If the copper is removed from the solution before the ferrous ion concentration has arrived at a high value, reaction (1) will slowly occur, leaving the final solution containing only oxidized iron. By decreasing the copper surface, reaction (3) can be caused to bring the final nitrate concentration to a lower value, although the rate of reaction is considerably decreased thereby. Also, by increasing the temperature, the same effect is noted because the increase in rate of reaction (3), with rising temperature, is greater than that of reaction (4).

DATA CONCERNING REACTIONS (3) and (4):

The following experiments illustrate the effect of temperature, copper surface, and nitric oxide concentration upon reaction (3):

Experiment (1). To each of several 10 c.c. portions of oxidized spent electrolyte containing 1.2 mg. of NO, were added one foot of #18 Copper wire, and they were placed in various temperature baths:

Temperature	Time for Reaction	Final NO <sub>2</sub> Conc.
50° C	3 Hrs.	4.0 g/l
60° C	50 Min.	2.3 g/l
70° C	30 Min.	2.0 g/l
80° C	30 Min.	1.2 g/l
80° C	25 Min.	1.8 g/l (This soln. was agitated.)

Experiment (2). With 100 c.c. portions of oxidized Spent Electrolyte, each containing 20 mg of NO, the following results were obtained at 80° C:

Length of #18 Cu wire used	Time for reaction	Final $\text{NO}_3^-$ conc.	Final $\text{Fe}^{++}$ conc.	Acid Loss
2.0 ft.	120 Min.	0.2 g/l	0.37 g/l	1.2 g/l
4.0 ft.	80 Min.	0.4 g/l	0.75 g/l	0.8 g/l
8.0 ft.	40 Min.	0.8 g/l	0.98 g/l	0.2 g/l

Experiment (3). To 10 c.c. portions of test solution varying amounts of nitric oxide were added and they were kept at 60° C.

NO used	Time for Reaction	Final $\text{NO}_3^-$ Conc.
2.0 g/l	2.0 Hrs.	1.1 g/l
2.5 g/l	1.5 Hrs.	1.1 g/l
2.9 g/l	1.0 Hrs.	1.1 g/l

SUMMARY CONCERNING REACTIONS (3) AND (4):

The amount of nitrate removed by reaction (3) varies directly with the temperature and inversely with the copper surface. The rate of reaction (3) varies directly with the temperature, the copper surface, the concentration of nitric oxide, hydrogen ion, and nitrate, and inversely with the concentration of ferrous ion and dissolved salts. Agitating the solution results in a decrease in both rate and nitrate removed.

ACID LOSSES:

It was noted, if copper is allowed to remain long in contact with the solution, after reaction (3) has ceased, that more than the stoichiometric quantity of hydrogen ion is used. This acid loss was found to vary directly with the initial acid concentration. For instance, with a solution containing originally 4.0 g/l of nitrate, 1.5 g/l of ferrous ion and 70 g/l of sulphuric acid, an excess of 60 % of acid is consumed. With a solution similar to this one, except that it contained 20 g/l of acid, just the stoichiometric

quantity of acid was used. Dissolved salts also tend to diminish this acid loss. The acid loss tends to decrease if the copper surface is kept to a minimum.

#### Absorption and Diffusion of Nitric Oxide

Since nitric oxide plays such a vital role in both reactions (1) and (3), it was thought desirable to get a semi quantitative idea of its solubility in solution. A glass tube  $1\frac{1}{2}$ " X 24" is filled full of glass beads, and solution at  $25^{\circ}\text{C}$ .<sup>is</sup> trickled at a rate of 10 c.c. per minute down the tube countercurrent to a slowly moving stream of nitric oxide gas. It was found that the test solution absorbed the most nitric oxide, the spent electrolyte absorbed a little less, and water absorbed only a trace of the gas.

At  $20^{\circ}\text{C}$ ., very little nitric oxide diffuses out of solution in two hours; after six to eight hours, however, most of the nitric oxide has disappeared. At  $60^{\circ}\text{C}$  most of the nitric oxide has left the solution in two hours, while at  $80^{\circ}\text{C}$ ., only one hour is required for the same amount of loss.

#### Denitrification by a Continuous Process

In order to oxidize the ferrous ion in the untreated spent electrolyte, the solution at  $25^{\circ}\text{C}$ . is first saturated with nitric oxide by being passed down a glass absorption tube similar to the one used above in the experiments on the absorption of nitric oxide. It is then introduced into the bottom of a test tube (volume 120 c.c.) which is filled with silica gel and immersed in a constant temperature bath. The solution coming from this tube contains no ferrous iron and is saturated with nitric oxide, due to the initial treatment and to the



nitric oxide formed during the oxidation of the iron; therefore it is in a condition suitable for reaction (3) to occur. It is passed into the bottom of a large test tube (volume 200 c.c.), containing ten feet of #18 copper wire, where reaction (3) is partially completed. Then it is passed into the top of another test tube (volume 200 c.c.) containing five feet of #18 copper wire, where its nitrate concentration is reduced to a minimum. Both of these test tubes are immersed in a constant temperature bath. The nitric oxide gas formed during these reactions is collected and utilized in initially saturating the solution in the absorbing tube. If the solution passes thru the system too fast, not enough nitric acid is removed; if the movement is too slow, the rate of reaction (3) is greatly retarded, and acid losses result from long contact with copper. Hence the problem is to adjust the flow so that the maximum amount of nitric acid is removed, without reducing the iron.

On further experimenting, a system was discovered which would oxidize the solution faster than had been possible previously with the silica gel tube. In this system, the solution, saturated with nitric oxide as before, is passed into the bottom of a test tube (volume 120 c.c.) containing solution in which the ferrous to nitrate ratio is very low; no solid catalyst is present. Immediately upon striking the solution the reaction occurs and nitric oxide is formed, rising to the surface in the form of extremely small bubbles, <sup>and</sup> tending to keep the nitric oxide concentration in solution very high; hence this condition of the gas favors an increase in the rate of reaction. Later it was found that once nitric oxide is formed in the reaction tube, <sup>it is unnecessary to</sup> first saturate the solution with the gas. Instead, the untreated solution is passed directly into the bottom of a tube immersed in a

constant temperature bath, where it comes in contact with hot solution containing nitric oxide and no ferrous ion, and where reaction (1) readily occurs. At 60° C, with this system, 6 c.c. of spent electrolyte can be oxidized per minute while this capacity is doubled at 80° C. The silica gel tube of the same total volume will handle only one half this amount of solution. If the solution is first warmed in a heating coil before its introduction into the reaction tube, the rate decreases somewhat due to less effective absorption of nitric oxide in the hot incoming solution.

Using this latter system of oxidizing iron, and the previously mentioned scheme of further denitrifying the solution, it was found possible at 70° C. to reduce the nitrate concentration in the spent electrolyte <sup>from</sup> 4.0 g/l to less than 1.0 g/l. The amount of solution handled was one half liter per hour.

For best results with this continuous system of denitrification, it is essential that none of the solutions bearing nitric oxide, be agitated, as this tends to lower the concentration of the gas in them. Hence gas traps are used between each reaction tube in order that no large bubbles are sent to the bottom of any of the tubes. What is desired is a constant stream of very small bubbles of nitric oxide and this situation is found naturally to be the case in solutions wherein either reaction (1) or (3) is taking place.

#### Continuous Denitrification as applied to Spent Electrolyte obtained from leaching Ore.

One month was spent in leaching 240 pounds of Chuquicamata ore (labeled regular) in order to obtain a representative spent electrolyte solution; synthetic solutions were made in order to start the leach. During this time, two leaches (two thirds of a complete leach-

ing cycle) were completed, the spent electrolyte after each leach being obtained by electroplating the copper out of solution, using lead-antimony insoluble anodes, which were furnished by the Chile Exploration Co. Partial analysis of the resulting spent electrolyte solution showed:

H <sub>2</sub> SO <sub>4</sub>	63 g/l
HNO <sub>3</sub>	7.4 g/l
Cl <sup>-</sup>	0.24 g/l
Cu <sup>++</sup>	15.4 g/l
Fe <sup>++</sup>	0.13 g/l

It is to be noted that the acid concentration of this solution is 7 g/l lower than normal, a factor which should be unfavorable in the denitrification process, although this disadvantage is somewhat off-set by the relatively high nitric acid concentration (almost twice normal). Since the iron is in an almost completely reduced state the oxidation reaction tube, mentioned above, was not used. Instead the solution was warmed in a heating coil and introduced immediately into the bottom of the first tube containing copper, and from there the arrangement was identical with that described above. In order to start the reaction, 100 mg of nitric oxide was introduced with the first 200 c.c. of solution treated. From then on the reaction proceeded well in both tubes containing copper, without the need of an outside source of nitric oxide; in fact all of this gas formed was allowed to escape into the air. Solution was handled at the rate of  $\frac{1}{2}$  l/hr. at 70° C, and the nitrate concentration was reduced to 1.2 g/l. By circulating the solution more slowly, or by adding additional copper, the nitrate concentration can be lowered to 0.7 g/l with ease. No acid loss results.

Thus, a system has been developed which requires trial on a large scale before its introduction into the present leaching cycle. It is believed that by denitrifying the spent electrolyte, the nitric acid content of the strong solution will be considerably reduced, and in time, the nitrate content of the system as a whole will be lowered to a low value which will insure a longer life to the anodes. Were this denitrification carried out in the strong solution, trouble might result in the electrolytic tanks due to solutions fouled with nitric oxide, unless special care were taken to remove the gas. By denitrifying the spent electrolyte instead, which is, in regard to time, further removed from the electrolytic tanks, there is less chance for foul solutions at the tanks. Also, since the volume of spent electrolyte <sup>is</sup> four fifths ~~is~~ that of the strong solution, less solution will have to be treated for nitrate removal. However, the chief advantage of denitrifying the strong solution is the possibility of oxidizing the iron in this solution and thus eliminating the necessity of adding an additional oxidizing reagent. It is believed that the iron in the strong solution <sup>can</sup> ~~may~~ be oxidized by saturating this solution with nitric oxide, which is obtained from denitrifying the spent electrolyte, and allowing it to remain in contact with tailings from the ore until the iron is oxidized. It may be necessary to pass air also thru the solution during this time in order to insure oxidation. Heating the solution will be unnecessary.

#### Economic Data

Twenty-five to fifty dollars per ton could be spent for the elimination of nitric acid from leaching solutions. Heat is available from waste heat boilers in an amount of 650 to 700 tons of steam per day at a cost of 25¢ to 50¢ per ton, neglecting the installation cost

of the boilers. Copper is available at less than  $\frac{1}{2}\phi$  per pound. At present, 17,000 cubic meters of spent electrolyte are produced per day. Assuming this solution is heated from 35° c to 70° c and only 2 g/l of nitrate are removed during each denitrification (this is a very conservative figure), an estimate shows that the cost of steam of nitric acid removed per ton is five dollars and the cost of copper is fifteen dollars. Assuming direct heating with steam and no heat loss, 650 tons of steam are required to heat 17,000 cubic meters of solution. Hence enough steam is available, assuming heat losses, to heat at least one half of the solution, which is more than the amount used in the lime-rock process; and the cost of removing nitric acid, assuming only 2 g/l removed, is twenty dollars per ton as compared with an allowable cost of twenty-five to fifty dollars per ton.

The actual equipment needed for carrying on denitrification would be merely a series of large tanks composed of a nitric acid resisting material, in which copper could be suspended, and a system of preheaters and heaters for bringing the solution up to temperature. Also, the cost of waste heat boilers must be included in the initial installation. No moving parts are required. No data is available on the cost of equipment, but, since this initial cost is to be divided thruout a period of years, it seems that the cost of removal of nitric acid would not exceed thirty-five dollars per ton. Thus the process seems practical both economically and technically.

Summary Sheet.

A system has been developed for the denitrification of the spent electrolyte derived from copper solutions obtained from leaching Chuquicamata copper ores, by means of reducing the nitric acid present with metallic copper in the presence of the catalyst, nitric oxide.

During denitrification it is essential that the iron which the solution contains be kept in the ferric form and that a high concentration of nitric oxide be maintained. This is accomplished by first causing the iron to be oxidized with the nitric acid present, by introducing the untreated solution into a vessel containing solution heated to 60° to 80° C., which is saturated with nitric oxide and which contains no ferrous iron. Then the solution is placed in contact with copper <sup>and</sup> ~~where~~ the metal dissolves, reducing nitric acid to nitric oxide. The ratio of the surface of copper to the volume of solution being treated must be adjusted. If this ratio is too high, ferrous iron will be formed more rapidly than it can be oxidized by nitric acid and consequently the reaction will stop; if the ratio is too low, not enough nitric acid will be removed.

With this system, using a copper to solution ratio of about .013 reciprocal centimeters, at 70° C the concentration of nitric acid is reduced from 4.0 g/l to less than 1.0 g/l at a rate of about 4 c.c. of solution per minute per square centimeter of exposed copper surface. The process is practical both technically and economically.

## A C K N O W L E D G M E N T

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