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CATALYTIC PRECIPITATION OF NICKEL, COBALT AND ZINC SULFIDES FROM DILUTE ACID SOLUTIONS

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This invention is concerned with the hydrometallurgical production of metallic cobalt and nickel, particularly from non-sulfide ores. Still more particularly, the present invention is concerned with a method of concentrating the nickel and cobalt values of non-sulfide ores while separating them from iron, aluminum, and other non-ferrous metals by selective precipitation from acidic leach liquors using hydrogen sulfide and a suitable catalyst.

In my copending application with F. A. Schaufelberger for United States Letters Patent, Serial No. 438,316, filed June 21, 1954, entitled "Precipitation of Non-Ferrous Metal Sulfides from Acidic Solutions," it has been shown that aqueous acidic leach liquors can be treated to precipitate cobalt and nickel values as their sulfides. This is accomplished by adjusting the acid content of the liquor followed by treatment at elevated temperatures with a nucleating agent under a relatively high overpressure of hydrogen sulfide.

It is not always possible or desirable to carry out the process at these conditions. It is, therefore, the purpose of the present invention to devise a process which is capable of selectively precipitating dissolved non-ferrous metal values from an acidic liquor at lower temperature and at lower contents of free acid. Such a process, to be considered successful, should recover at least 98% of the metal or metals of interest. Preferably the precipitate should not assay more than about 3–4% contaminant metals such as iron, aluminum, manganese, magnesium and the like which usually dissolve concomitantly with cobalt and nickel during leaching. Such a process also should be capable of precipitating substantially all of any zinc present in the leach liquor. Precipitation should be completely obtainable in a period of two hours and preferably less than one hour.

In the previously identified copending application, it was pointed out that using a high reaction temperature, above 90° C. and preferably from about 100° C. to about 150° C. or higher and a relatively high overpressure of H_2S was considered necessary. This was based on the well-known fact that nickel and cobalt cannot be precipitated as sulfides from a dilute aqueous acidic solution merely by the use of hydrogen sulfide under normal conditions. It was thought that the success of the process was definitely attributable to the use of the elevated temperature range at relatively high acidity, the use of a nucleating agent and the use of sufficient overpressure of hydrogen sulfide to build up the requisite sulfide ion concentration.

According to the present invention, it has been found that the desired result can be obtained successfully at lower temperature and acidity by the use of suitable catalyst material by treatment started at a temperature of from about 60°–65° C. in the presence of a small quantity of any finely-divided solid catalyst material. If so desired, the nucleating agent of the above-identified case may be used. Typical examples of the latter include graphite, kieselguhr or infusorial earth and the like, talc or finely

ground sulfides or oxides of one or more of the metals being precipitated.

As cobalt and nickel source material for the present invention, any liquor containing dissolved salts of the desired metals can be used. Of primary interest are such liquors obtained by leaching, usually acidic, of such ores as are variously referred to as lateritic, oxidized, siliceous, weathered-silicate or non-sulfide ores. For the purpose of this discussion, they will be referred to as non-sulfide ores because while otherwise varied, they are characterized by an absence of sulfur. They may be leached by any desired method which inherently or by subsequent adjustment produces an acidic solution.

Since sulfuric is the acid most commonly used in leaching on ores of this type, it too will be taken as illustrative. After leaching, an illustrative pregnant leach liquor might be found to contain the following dissolved content in grams per liter:

Ni	3.0–12.0
Co	0.2–0.7
Fe^{++}	0.5–2.0
Al	2.0–8.0
Mn	1.0–5.0
Mg	0.5–2.0
H_2SO_4	15–30

Although these values are not intended to be limiting on the process, discussion of such a solution will be taken as typical.

The process of the present invention is, of course, equally applicable to leach liquors obtained by the leaching of sulfide ores. However, it has less practical importance in that field because leaching methods are known for metal sulfide ores which provide leach liquors that do not require the treatment of the present invention. Whatever the source, the liquor can be advantageously treated by the process of the present invention, when it is desired to purify and concentrate the cobalt and nickel values into the smallest possible bulk for further treatment.

At the completion of leaching, which as noted may have been carried out in any desired manner, the final content of dissolved free acid may be and usually is too high for the purposes of the present invention. The first positive step, therefore, is to adjust the acid content of the liquor as may be required. It is undesirable to exceed an acid content of about 3–4% at any time, even at the end of the reaction. At this acidity the reaction rate becomes too slow. Some control must be exercised to insure against this occurrence which would prevent complete precipitation in the time available.

In this respect, the original solute content of the liquor is of important consideration in some cases. Consumption of hydrogen sulfide during reaction causes the acidic content of the liquor to increase as the metal sulfide precipitates. If the original metal salt content is sufficiently high, the resultant increase in acid concomitant with precipitation of the sulfide may result in exceeding the upper limiting factor.

Ordinarily, this necessity for controlling the terminal acid condition will not be too serious a problem. Perhaps the simplest approach is to adjust the initial pH to some value which will prevent the increase in acidity during reaction carrying the resultant acid content to too high a level. In general, this will be to an initial acid content not less than about pH 3.5. At higher pH values, precipitation is no longer sufficiently selective and other precipitates may be formed. Aluminum can be particularly troublesome. With ores frequently encountered in the field, the aluminum content which dissolves during leaching is fairly high. At a pH of about 3.5 it is

readily possible for aluminum hydroxide to exceed the solubility product and precipitate.

In general, therefore, it is undesirable to go above about pH 3.0 in the neutralizing step. Particularly is this true when operating a continuous flow scheme. When the process is operated on a batch basis it may be carried out at any pH at which hydroxides do not form. If the solution is treated on a batch basis it may be possible in some cases to go to an initial pH as high as 5 or 6. When the process approaches neutrality or basic conditions, particularly where ammonia in sufficient amounts to form ammoniacal complexes is used, the resultant slurry is particularly hard to filter and handle.

On the other hand, it is undesirable to have the initial pH much less than about 1.0. In general, the lower the acidity the faster the reaction rate and for an initial pH of less than about 1.0 the overall rate is apt to be slow. In general, then, the initial acid content adjustment, if necessary, will be to a pH of from about 1.0 to about 3.0. A preferred practice for the illustrative solutions would be from about 2.0 to about 2.5. Usually this will be adequate as an overall control. In the few cases where it is not, because of high metal content, the use of hydrogen sulfide may be supplemented by the use of some acid neutralizing agent such as ammonia or ammonium or sodium hydroxide. It may also be supplemented or replaced in whole or in part by a different source of sulfide ions. This may include using such reactants as sodium sulfide, ammonium sulfide or their chemical equivalents which will form soluble salts rather than free acid.

Generally, but not necessarily, neutralization will be carried out commercially with limestone or its equivalent. Since this introduces insolubles it will preferably be done before separation of the leach liquor from its accompanying solids. In some cases, as where no precipitate forms during neutralization or no insoluble is introduced, or where it is desirable to isolate any precipitate formed, neutralization may be carried out after decanting the leach liquor from the residual solids. In any case, leach liquor is separaed from accompanying solids, the latter usually being washed and clarified liquor with or without washings, is sent to subsequent treatment.

Of primary importance in the present process, is the utilization of a catalyst. The selection of a catalyst will depend to some extent upon the nature of the solution. Therefore, for this purpose in the present invention the same illustrative liquors obtained by sulfuric acid leaching of non-sulfide ores which are discussed above will be considered typical. A list of satisfactory catalysts for such a solution would include powdered metallic iron, nickel and mixtures of nickel and cobalt. Use of powdered iron as the catalyst does not present a combination problem. Since the sulfides product in any case is to be redissolved for further treatment, the small amount of iron added as catalyst is of no importance and can be easily eliminated in that treatment. Where speed of reaction is primarily important, freshly reduced iron powder, as the fastest acting catalyst, is perhaps to be preferred. However, it is less selective also and tends to produce in the sulfide precipitate a higher content of iron and aluminum compounds than when nickel and/or cobalt metal is used. Hydrogen gas can be used. But from a handling point of view, a gas is not as simple as the use of solids. In amount, the catalytic metal added for the purpose will usually range from about 0.03 to about 5 grams per liter. More can be used.

In addition to the added catalyst, it is highly desirable to add some seeding or nucleating agent. Probably the most useful material for this purpose is some of the product nickel sulfide or cobalt sulfide or mixture thereof which was produced in a previous run. This use of such added material may and usually does increase the rate of reaction to some extent. This is probably due to the presence of some catalyst material in diluted form. Of more practical importance is the fact that it reduces sulfides deposition on the walls of the pressure vessel in which the reaction is carried out. The more finely divided the recycled sulfides, the more effective. They should be minus 20 mesh and if possible, minus 200 mesh. A minus 200 plus 325 mesh fraction is excellent. A good practice is to grind and recycle some three to ten per cent of the product. Usually an average of about five per cent is a good practice for this purpose.

Another variable of importance in controlling the reaction is the temperature which is used. At ordinary ambient temperatures, reaction is very slow. When the temperature reaches about 60–65° C., the reaction rate becomes high enough for practical development. From 65° to about 90° C. the reaction rate is effective. However, increasing the temperature above about 90° C. does not cause the reaction rate to increase noticeably within the preferred range of acidity. Therefore, in most operations, the temperature at which reaction is started should be somewhere from about 60° to about 90° C. The reaction is exothermic to a considerable extent and once reaction has been started it is not at all difficult to maintain this temperature range. Thorough agitation is highly desirable.

Reverting to consideration of the catalyst material used, it should be noted that size is of more importance, generally, than the weight of catalyst material which is used. Therefore, it may be considered that the higher the degree of subdivision, the more active is the catalyst. In using a solid catalyst, in particular, it should be fed to the solution in the smallest practicably obtainable sizes. This not only increases the reaction rate but aids in preventing the objectionable deposition of sulfides on the wall of the vessel. It is also of interest to note that, unlike most cases, it is desirable that the particles have smooth surfaces, smooth, round particles being more effective than rough, irregular ones.

It is an interesting feature of the present invention that it is not affected adversely by sensitivity to the feed ratio of nickel to cobalt. In general, the process may be operated at any Ni:Co feed ratio ranging from 10:1, or more, in either direction.

The active reagent in the present process is hydrogen sulfide gas. It is obviously necessary that it be furnished in adequate quantities to produce in solution the necessary sulfide ion concentration. Other than this, there is little effect from varying the rate of feeding the gas. According to the present invention, it has been found that this sulfide ion concentration can be maintained by keeping a hydrogen sulfide overpressure on the solution in a closed vessel. The hydrogen sulfide should be bubbled in through the liquid below the surface. Successful results are obtained with pressures of about ten pounds per square inch gauge or more. H_2S pressures up to about 100 p. s. i. g. are readily obtainable. Pressures above this point probably have no really beneficial effect and are not necessary except at high acidity outside the preferred range.

In some cases, it may be questioned whether or not it is desirable to recycle the precipitate in building up the nickel:cobalt content of the sulfide precipitate. Where this is done, the recycle solid probably acts as noted above as an extender containing some catalyst metal. Generally, it will be found to have less active surface and excessive recycling may result in more plating on the walls than is desirable. In continuous operation, however, to provide for uniformity of operation, it may be desirable to recycle some of the product. Usually, if recycling for this purpose is done, it will amount to some 50 to 200% of the circulating load. In batch operation it is doubtful whether more than the small amount desired to provide seeding surfaces for the sulfides are needed or will be recycled.

With this discussion in mind, the principal points of the

process may be summarized as follows: adjusting the leach liquor, before or after removal of the undissolved tailings, to a pH of from about 1.5 to about 3.0 and separation of resultant liquor from solids, the latter being washed and the washings either added to the liquor or recycled to leaching; placing clarified leached liquor in a suitable pressure vessel; adding thereto a small amount of catalytic iron, cobalt and/or nickel metal powder; subjecting the resultant mixture, with or without a recycled amount of ground, previously precipitated sulfides to agitation under a hydrogen sulfide overpressure of from about 10 to 100 p. s. i. g. or more at an initial temperature of from about 60° C. up to about 90° C. and continuing the reaction until the dissolved content of nickel and/or cobalt is sufficiently lowered.

Subsequently the sulfide precipitate is de-watered and washed. If so desired, the sulfide is collected by froth flotation or the like. Collected sulfides are then subjected to further processing in which the cobalt and/or nickel content thereof is recovered. These latter steps are not part of the process of the instant invention.

It is a feature of the present process that any manganese, magnesium, calcium and chromium content of the solution, together with substantially all the dissolved iron and aluminum, remain in the solution. Cobalt and the nickel are substantially completely precipitated therefrom. When zinc is present it will be precipitated with the cobalt and/or nickel but is easily separated in the subsequent production of metal. If so desired, the liquor can be subsequently processed to recover one or more of these metals. Such treatment forms no part of the present invention.

The process of the present invention will be illustrated by the following examples which are intended as illustrative only and not by way of limitation. In these examples, the concentration of dissolved metals is calculated for the metal content only and is indicated in grams per liter (g./l.). All parts are by weight unless otherwise noted.

EXAMPLE 1

A sample of Cuban lateritic ore is subjected to a high-temperature sulfuric acid leaching. Decanted leach liquor contains the following dissolved metal content in grams per liter (g./l.): Ni—5.6, Co—0.46, Fe^{++}—1.1, Al—5.9, Mn—3.2, Mg—1.1, and free H_2SO_4—15. A 1500 ml. sample of the solution is placed in an open vessel, neutralized to a pH of 1.5 with soda ash, heated to 65° C. and hydrogen sulfide gas bubbled therethrough for one hour. No precipitation of sulfides whatever is obtained.

EXAMPLE 2

Another one liter sample of the leach liquor of Example 1 is heated in an open vessel to an initial temperature of 65° C. and H_2S bubbled therethrough for one hour in the presence of five grams of fine powdered nickel metal (100–325 mesh). At the end of one hour, 42% of the nickel and 39% of the cobalt are precipitated as their sulfides.

EXAMPLE 3

Example 2 is repeated placing 1500 ml. of the solution in a pressure vessel equipped for agitation and subjected to a 25 p. s. i. g. overpressure of H_2S and 2.5 gms. per liter of nickel powder obtained by hydrogen reduction of nickel diammine sulfate solution. At the end of a one hour reduction, a precipitate is obtained containing 67.8% Ni, 3.8% Co, 0.036% Al, 0.65% Fe, 28% sulfur and a trace of manganese. The filtrate contains only 0.04 g./l. of nickel and 0.01 g./l. of cobalt.

EXAMPLE 4

A sample of the residual tailing solids after the leaching step of Example 1 is ground to minus 325 mesh and then reduced with hydrogen for two hours at 800° C. and resultant solid precipitate of fine iron powder particles (averaging from 5 to 20 microns diameter) is collected.

A one and one-half liter sample of the solution of Example 1 is adjusted to pH 1.5 with soda ash; 1.7 grams of the reduced iron powder is added, the mixture heated to 65° C. and reduced in a pressure vessel under a hydrogen sulfide over-pressure of 25 p. s. i. g. for 90 minutes with agitation by a propeller-type stirrer turned at 600 R. P. M. Both precipitate and filtrate are analyzed. Precipitation is 99% complete as to cobalt and nickel, the filtrate analyzing 0.049 g./l. nickel and 0.0046 g./l. cobalt. The precipitate analyzes as follows: Ni—53.25%, Fe—4.62%, Al—0.65%, Mn—less than 0.01%.

The preceding example shows the efficiency of the iron powder in producing complete precipitation in the desired degree in a short time. However, it will be noted that the solids produced contain a moderately high content of iron and aluminum. That a solid precipitate lower in iron can be obtained using cobalt and/or nickel as the additive is shown in the following examples.

EXAMPLE 5

A sulfide precipitate was prepared by repeating the procedure of Example 3. Collected precipitate was roasted in air for one hour at 600° C. The resultant calcine is reduced with hydrogen for two hours at 400° C., yielding a finely divided cobalt-nickel mixed metal.

To 1.5 liters of the leach liquor of Example 1 is added sufficient sodium carbonate to produce a pH of about 1.5. To resultant solution is added 1.7 grams of the reduced nickel-cobalt powder. The mixture is placed in an autoclave under 25 p. s. i. g. overpressure of hydrogen sulfide and at an initial temperature of 65° C. The mixture is treated with agitation for about two hours. At the end of the period, 99.4% of the cobalt and 98.4% of the nickel is precipitated as a rapidly-filtering sulfide residue. Analysis of the residue is as follows: Ni—57.9%, Co—4.7%, Fe—1.2%, Al—0.36%, Mn—0.001%.

EXAMPLE 6

In order to show the effect of varying the initial reduction temperature, a series of sample of an aqueous sulfuric acid leach liquor containing 5.1 grams per liter of nickel (as sulfate) are reduced to an initial pH of about 2.0, seeded with 0.5 g./l. of nickel seed powder (produced as in Example 5) and treated under about 25 p. s. i. g. H_2S overpressure for varying periods of time. In one series, the intial reduction temperature is at ambient temperature; the second at 65° C. and the third at 90° C. At periodic intervals, the nickel content of the solution is examined. Typical results are summarized in the following Table I.

Table I

[Residual dissolved Ni content (g./l.)]

Initial Temp. (° C.)	Elapsed Time (Minutes)				
	10	20	40	60	80
Ambient	5.0	4.9	4.8	4.7	4.65
65	3.8	2.7	1.4	0.8	0.5
90	0.9	0.3	0.1	0.07	0.05

EXAMPLE 7

In order to show the effect of the initial pH on nickel sulfide precipitation, a number of samples of an aqueous acidic leach liquor initially containing 5.8 g./l. nickel are seeded with 0.5 gram per liter of nickel powder (produced according to Example 3) and reduced under 25 p. s. i. of hydrogen sulfide from an initial temperature of 65° C. The residual liquor is examined at periodic intervals to determine its residual nickel content. The initial

pH is varied in succeeding series. Typical results are summarized in the following table.

Table II

[Residual dissolved Ni content (g./l.)]

Initial pH	Time (Minutes)			
	10	20	40	60
1.5	2.76	1.49	0.38	0.10
2.0	1.12	0.51	0.16	0.06
2.5	0.62	0.18	0.06	0.02

EXAMPLE 8

To illustrate the effect of varying the pH on cobalt sulfide precipitation, a sample of leach liquor containing initially about 0.47 gram per liter of cobalt is divided into a number of portions, each of which is seeded with about 1 gram per liter of iron powder produced as in Example 4 above and from an initial temperature of 65° C. reduced for varied lengths of time. In the first series, the initial pH is about 1.5; in the second, about 2.0 and in the third, about 2.5. Typical results are shown in the following Table III.

Table III

[Residual dissolved Co content (g./l.)]

Initial pH	Time (Minutes)				
	10	20	40	60	80
1.5	0.18	0.08	0.02+	0.01+	0.01
2.0	0.15	0.03	0.003	0.001	------
2.5	0.08	0.01	0.001	------	------

EXAMPLE 9

In order to show the effect on the rate of nickel sulfide precipitation of varying types of solid additives, a number of samples of the leach liquor of Example 1 are neutralized with soda ash to an initial pH of about 2.0 and from an initial temperature of 65° C. and under an H_2S overpressure of 25 p. s. i. are reduced for varying lengths of time, the residual nickel concentration of the solution being periodically examined. Illustrative results are shown in the following Table IV.

Table IV

[Residual dissolved Ni content (g./l.)]

Solid Added	Time (Minutes)				
	10	20	40	60	80
90% Ni S 10% Co S } 2.5 g./l.	4.2	2.9	1.2+	0.7+	0.5+
Ni—1.0 g./l.	2.5	1.1	0.31	0.11	0.08
Fe—1.0 g./l.	1.2	0.5	0.15	0.06	0.03

I claim:

1. In the hydrometallurgical production of nickel and cobalt wherein non-sulfide ores containing nickel, cobalt and iron are leached with an aqueous acid liquor and the cobalt and nickel content of the leach liquor is chemically precipitated, the improved method of concentrating and separating nickel and cobalt from iron and other non-ferrous metal impurities which comprises the steps of: adding sufficient acid-neutralizing agent to adjust the free acid content of the liquor to a pH of from about 1.0 to about 3.0; adding to so-treated liquor from about 0.03 to about 10 grams per liter of a material selected from the group consisting of finely divided iron, nickel, cobalt and mixtures thereof; placing the mixture at a temperature of from about 60° C. to about 90° C. under a positive overpressure of hydrogen sulfide gas and continuing treatment with agitation until sulfide precipitation substantially ceases.

2. A process according to claim 1 in which the liquor is clarified after the neutralization step.

3. A process according to claim 1 in which the initial neutralization is to a pH of from about 2 to about 2.5.

4. A process according to claim 1 in which the powdered metal additive is an iron powder of from about 5 to 50 microns average diameter.

5. A process according to claim 1 in which the solid additive is a nickel metal powder.

6. A process according to claim 1 in which the solid additive is a mixture of finely divided nickel and cobalt metal powders.

7. A process according to claim 1 in which the solid additive is supplemented by at least one material selected from the group consisting of finely-divided cobalt sulfide, nickel sulfide, and mixtures thereof.

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