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Laboratory methods for copper-nickel ores

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LABORATORY METHODS FOR COPPER – NICKEL ORES

by

Walter I. Phillips

(An account of the laboratory methods of the Canadian
Copper Company, Copper Cliff, Ontario, Canada.)

MISSOURI SCHOOL OF MINES AND METALLURGY,

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The Sudbury nickel field, situated in the Province of
Ontario, Canada, near the northern shore of Lake Huron, was prac-
tically discovered when building the Canadian Pacific Railway.
The method of deposit is unusual in that it is not a vein filling
but a true igneous deposition. The magma carried besides rock
making constituents three principle sulphides, viz. - those of
iron as pyrrhotite; of copper as chalcopyrite; and of nickel as
pentlandite. These three sulphides, being heavier than the rock
matter, and, favored by the slow rate of cooling of the magma, had
sufficient time to settle into the lowest portions of the mass,
thus forming an igneous deposition.

Character of the Sudbury Ores.

"The ores of the Sudbury mining district are extraordi-
narily uniform, three sulphides only making up practically the
whole of most of the ore bodies, and only two as a rule presenting
themselves to the eye, pyrrhotite or magnetic pyrites, and chalco-
pyrite or copper pyrites. The third one, pentlandite, is much the
most important, though commonly invisible in the ore except at a
few of the richer mines, where it appears only occasionally.

"The mineral present in much the largest amount is pyrr-
hotite, a sulphide of iron whose composition as given varies from
Fe_5S_6 to $Fe_{16}S_{17}$. It is pale bronze with bright metallic lustre

Report of Bureau of Mines on Sudbury Nickel Fields, 1905.

"on fresh surfaces, but quickly tarnishes to brown, and very readily weathers, turning to a rusty mass, the gossan which is so characteristic of all the nickel mines. It almost never appears in crystals, though a certain platy character at a few mines suggests crystalline structure, and it may be from coarse to fine-grained. Its property of magnetism distinguishes it from other sulphides, since it is easily attracted by the magnet, while others are not, but the strength of its magnetism varies considerably in different localities, for reasons not certainly understood.

"In a few places pyrrhotite has occurred almost to the exclusion of copper pyrites, where there was so little copper in the ore that plans were made at the Sault Ste. Marie for roasting it, and reducing the resulting oxide directly to ferro-nickel; but even at these places, mining operations soon showed a considerable amount of chalcopyrite, making the ore unsuitable for that purpose.

"Though the chalcopyrite is generally present in much less quantity than the pyrrhotite, occasionally, as at the Copper Cliff in early days, it may form the larger proportion of the ore. The two sulphides commonly occur together, the brassy lustre of the chalcopyrite distinguishing it from the bronze of the pyrrhotite, and polished surfaces of ore show quite irregular arrangements of the two minerals. They do not appear to be very minutely intermixed as a rule however, and it is not difficult to select fairly pure examples of each.

"Pure pyrrhotite contains on the average about 3.21 per cent. of nickel in the Sudbury region, and pure copper pyrites, having the composition CuFeS2, contains 34.5 per cent. of copper. Since the ores of the district produce on the whole about equal amounts of the two metals, the proportions of the two minerals in the ore must be about 10 parts of pyrrhotite to one of chalcopyrite.

"The variations in the proportions of the two minerals even in the same ore body are sometimes wide, as at Copper Cliff, where the percentages obtained in different years present differences such as 4.65 copper to 4.46 nickel at one time and 7.81 copper to 2.37 nickel at another. The different mines vary even more widely from one another in this respect, the Creighton, for example, having nearly 5 per cent. of nickel to 2 of copper, in contrast to the percentage given above for Copper Cliff.

"It is probable that the chalcopyrite is a little more mobile in the ore bodies than the pyrrhotite, since it is more commonly found filling fissures in the country rock, or as a film between slickensided surfaces of the later diabase dikes. It has been observed also that at Copper Cliff the ore body was richer in copper when narrow, and in nickel when wide, so that the relations to the adjoining rocks appear to have some influence on the distribution of the two minerals.

"The third and most important mineral is pentlandite, a rich ore of nickel, having the composition (Fe,Ni) S, with a varying

"amount of nickel sometimes reaching 35 per cent. or more. It is not easily distinguished from the pyrrhotite in which it is embedded in fresh ore, the main difference being its rather perfect octahedral cleavage, but its brassy lustre on slightly weathered surfaces is characteristic. It has been found in a number of the mines, probably because too finely disseminated; but at Creighton, Worthington, Evans and a few other deposits, it sometimes occurs with cleavages half an inch wide. As experiments carried out by several persons have proved that with fine crushing a magnet will separate a more magnetic part with little nickel from a less magnetic part rich in nickel, it seems probable that most if not all of the nickel is contained in pentlandite, which is non-magnetic, and that the pure pyrrhotite would be found to contain little or no nickel.

"Iron pyrites in both its varieties is not infrequent in the ore deposits, sometimes as distinct octahedral crystals enclosed in pyrrhotite, sometimes in larger quantities with no crystal forms and belonging to the variety marcasite. In the latter case it may contain a considerable percentage of nickel.

"Several other compounds of sulphur and arsenic with iron and nickel occur in the deposits, but in such small quantities as to have no importance as ores."

The ore always occurs with noirite, the rest of the country rock being quartz with orthoclase frequently present.

Sampling and Assaying.

The ore from the mines is shipped directly to the smelter where it is sampled following the usual method of crushers, and rolls to the bucking board where it is quartered and bucked down to pass through a ninety mesh screen, but with mattes a one hundred and ten mesh screen is more satisfactory.

A fifteen gram sample is delivered to the laboratory, from which one-half gram is taken for assay and fused with three grams of potassium bisulphate in a two inch porcelain evaporating dish. When fusion is quiet it is removed from the fire and the dish given a gentle rotary motion in order to spread the fusion on the sides as it cools. When treated in this manner the now cold fusion readily falls out when the inverted dish is tapped on the bottom. The fusion is dissolved in a No. 2 Jena beaker with a few drops of HCl and sixty cc hot water, then the insolubles are filtered off, using a 325 cc straight beaker for the filtrate. The residue is washed free from acid. Neutralize with NH_4OH and then make barely acid with HCl and precipitate the copper with H_2S. Filter into No. 5 beaker, wash seven to eight times, with hot H_2O. Spread the paper and wash the precipitated copper back into original beaker in which the precipitation was made. Clean the paper with bromine water, add HNO_3 and evaporate almost dry, fusing the sulphur, but avoid spitting. Wash the sides of the beaker with a little water, neutralize with Na_2CO_3 solution till blue $CuCO_3$ remains

undissolved, acidify with acetic acid, add KI, and titrate with sodium hyposulphite.

Many chemists recommend boiling the copper solutions with $Na_2S_2O_3$ in order to completely precipitate the copper, but with our ores and mattes it was found sufficiently accurate and quicker to use the H_2S gas, and the results compared favorably with those obtained by the electrolytic method.

To the filtrate containing nickel add two or three cc HCl, boil off H_2S and oxidize the iron with $KClO_3$, remove from the heat, add ten cc sodium citrate, make slightly ammoniacal, cool and titrate with KCN, after adding five cc of $AgNO_3$ solution and five cc KI. (The AgI formed is simply an indicator, being insoluble in a weak ammoniacal solution and is dissolved by the last drop of KCN.)

Manganese and zinc interfere with the nickel determination but as our ores carried only a trace of those metals no thoroughly tested method has been worked out for eliminating them, as far as I am aware. Experiments with solutions containing zinc and nickel salts showed that zinc had a very uncertain effect on the cyanide.

Cobalt is counted as nickel in this method, and since it is a desirable metal no effort has been made to eliminate it.

Mattes.

Furnace and converter mattes are dissolved directly by HCl and then run exactly as the ores except that they are not

neutralized with ammonia and the solution is diluted directly till the acid is approximately 1:3.

The following short cut is, at times, resorted to with converter mattes when rapidity of manipulation is the most important factor. Weigh one-half gram into a dried 400 cc beaker, add about four grams KClO4 and mix by shaking, then add ten cc HNO3 and put on high heat. When sulphur is all dissolved, raise the cover and take to dryness. Moisten twice with HCl to expel the HNO3. Take up in five cc HCl and twenty cc H2O and proceed as usual for the determination of copper and nickel. By this method forty-five minutes is saved in getting the matte into solution, less acid is required and the final bulk of the solution is smaller than when the regular method is used, and the assays are equally reliable. By the other method the attention required when getting the matte into solution is materially less and the annoyance caused by the harmless explosions of fumes from the KClO4 is avoided.

Slags.

Converter slags readily yield to the same treatment as the ores but with furnace slags weigh out two grams of slag and brush into a small platinum evaporating dish. Moisten with a little H2O, add four cc dilute H2SO4 (1:1), ten cc HF and one cc HNO3. When violent action has ceased, evaporate to fumes on the low heat.

Take up in dilute HCl, warm and transfer to 325 cc beaker. Add seven to eight drops HNO3, and boil to small bulk, - about fifty cc or less, to insure that the nitric acid is driven off.

Cool, transfer to separating funnel and make ether sepa-

ration for iron.   Boil off the ether, and reduce the bulk as low
as may be desired.   Cool, add ammonia till the aluminum just pre-
cipitates.   Add HCl till the aluminum just dissolves, and then
two cc excess of acid and proceed as usual for copper and nickel.

This process requires considerable time and the precip-
itated calcium sulphate is particularly annoying, greatly augment-
ing the tendency of the slags to "spit" at each evaporation.   An
unsuccessful attempt was made to avoid this trouble by omitting the
addition of H_2SO_4 at the beginning, and using HCl and HNO_3 only
with the HF.   The alteration did not appear to effect the volati-
lization of the SiO_2, but later when the nickel solution became
ammoniacal it was found impossible to keep the $Al(OH)_3$ completely
in solution regardless of the amount of sodium citrate present.
When H_2SO_4 was again resorted to the aluminum gave no trouble,
thus showing the necessity of having soluble sulphates present in
order to keep the large amounts of aluminum from precipitating out
of ammoniacal solutions.

Electrolytic Determinations.

Copper is determined electrolytically by the nitric acid
method.   It is precipitated by H_2S as usual.   Dissolve the copper
in HNO_3, add two cc, dilute H_2SO_4 (1:1), and take down to fumes and
precipitate will be white when HNO_3 is entirely driven off.   Add
twenty drops HNO_3 and twenty cc H_2O, boil.   Filter on ashless filter
to remove the sulphur and wash.   Cool, put on battery and dilute

till cathodes are just covered plate at two amperes using current density - 0.16 amperes per 100 sq. cm. Voltage - 64. Time - 15 hours. The cathodes used were cylindrical in form and the anodes spiral.

Nickel is determined in the filtrate from which the copper was precipitated. After boiling off the hydrogen sulphide the iron is oxidized by a few drops of $H2O2$ and the solution made ammoniacal and from thirty to fifty cc of NH4OH in excess added, and then twenty-five cc of a cold $(NH4)2SO4$ solution. (This latter solution is made by adding concentrated $H2SO4$ to one hundred cc of cold water till the beaker feels hot to the hand, and then made strongly ammoniacal.) Put the nickel solution on the battery with the same apparatus as when plating copper using a current density - 1.18 amperes per 100 sq. cm., voltage - 64. After twelve hours, when the solution has become colorless, add more NH4OH and heat to about 75° C in order to hasten the precipitation. From time to time a few drops of the solution are tested with potassium sulphocarbonate, and when the delicate rose red color no longer appears the operation is completed and the cathode removed from the battery, dried and weighed.

Cobalt plates with the nickel, and the nickel is determined by redissolving the two metals from the cathode with HNO3 and the cobalt is precipitated by the standard potassium nitrite method and replated, and the nickel obtained by difference.

Experiments conducted up to the time I was in the laboratory of the Canadian Copper Company had not developed any reliable short cut for the electrolytic determination of cobalt in the presence of nickel and the precipitation of cobalt by KNO2 cannot be reduced much under twenty-four hours. At best this method for nickel is long and tedious but when correctly done the results are very accurate.

Zinc has not been electrolytically separated from nickel and it occupies the same unsatisfactory status here that it does in the volumetric methods.

Nickel cannot be quantitatively separated from iron in four or five successive precipitations by ammonia even when the iron is as low as one per cent, and where the iron in the ores or mattes is over three per cent it is best to make an ether separation before plating the nickel. In the volumetric method an ether separation for iron is not necessary when the iron is as high as forty-one per cent.

The bulky precipitate of iron in the ammoniacal nickel solution seems to mechanically hold small amounts of the nickel, and the iron salt, being a poor conductor of the current, probably prevents any electrolytic action on the nickel solution so enclosed, thus giving a low result.

Aluminum probably acts in a similar way towards the nickel solution as the iron, for considerable trouble has been

experienced in the electrolytic determination of nickel in slags
where the Al2O3 ran as high as .16 grams.   The ether separation
does not effect the aluminum which becomes a bulky precipitate in
the ammoniacal solution of the nickel.

No account is taken of whether or not a trace of iron
is co-precipitated with the nickel when making analyses for commer-
cial purposes, the amount, if any, being regarded as too small.

In comparing the volumetric with the electrolytic method
for nickel the former is rapid and sufficiently accurate for routine
work and probably is more accurate on ores and slags that are high
in aluminum, but the electrolytic method is regarded as the standard
on high grade mattes, and the selling price is based on those as-
says.   The solutions used in the wet determinations are always
standardized on bessemer mattes which have been assayed electroly-
tically.

Bibliography.

A. .P. Coleman. - Report of the Bureau of Mines, 1905,
Vol. XIV - Part III.   Toronto, Ontario, Canada.
This is an excellent account of the geology of the Sudbury
Nickel Field and history of its development.

Sutton's Volumetric Analyses.
This book gives a very complete account of the volumetric method
for nickel.

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