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THE LAKE SUPERIOR FIRE ASSAY FOR COPPER.

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As THIS method has been practically omitted from the latest editions of Peters' "Modern Copper Smelting," because of the superabundance of metallurgical material of wider interest, and as no full description has been published since the original paper of Mr. M. B. Patch was printed, many years ago, it may be of advantage to students, and to assayers, to place on record the details of present practice in refineries and stamp mills of the Lake Superior district.

The assay is adapted only to native copper occurring in veins, or bedded deposits, including the milled concentrates from the same, and also any oxides, carbonates or silicates of copper, if entirely free from sulphur. While Mr. A. H. Low,[1] of Denver, has been very successful in perfecting the "cyanide" and "iodide" assays of copper ores they are not as well adapted to native copper products[2] as the "electrolytic" assay or the Lake Superior crucible "fire assay."

In the lake region, choice of method is made according to the coarseness and richness of the sample to be treated and the tech-

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[1] Peters' "Modern Copper Smelting," latest edition.

[2] *Eng. Min. J.* (1895), pp. 369 and 387.

nical accuracy required. The Heine Blue Test,[1] improved by the writer and others, is suited for rapid working tests of poor slags and tailings under 1.5 per cent. copper. For accurate work on material easily sampled, the battery assay[2] is employed, with special modifications when applied to refined copper.[3]

SAMPLING OF MATERIALS CONTAINING NATIVE COPPER.

The estimation of the metal may be required in:

I. Mine rock, as hoisted from prospecting shafts;
II. Mill concentrates, gravels and tailings;
III. Rich reverberatory furnace slags;
IV. Waste slag from "slag remelting" cupolas.

I. The low grade vein rock of the mines is well understood to carry the metal in particles of such uneven size, so unevenly disseminated in the lode, that any valuation of even a stope on anything short of a mill test of 100 to 500 tons, is of no practical value. An approximate test of any particular carload might be made by crushing to chestnut size, sampling down, grinding several pounds with repeated siftings, picking out and weighing separately the shots left on each sieve, and fusing 0.25 to 1 pound of the remaining fines in a crucible with appropriate fluxes.

II. According to the writer's experience, the "battery assay" of rich concentrates does not give as good results in the long run as the "fire assay," even if a large sample is dissolved in acid and an aliquot part by volume of the solution is taken for the electrolysis. Results would be better if aliquot parts were taken by weight, for the multiplication of slight errors in measuring flasks tends to make the result rather inaccurate.

Rich coarse material can not be accurately sampled for 1000 grain assay, when very dry, but should be wet sufficiently to make the particles adhere and a sample taken out of the material for a water determination, just before the one for copper. At refineries, concentrates are sampled by the furnace men, either at the shutes when filling hand-carts, or from the mixed pile on the charging floor of the furnace, the sample being preserved in tightly covered tin-lined copper cans.

At the C. and H. Stamp Mills, coarse gravels and other non-

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[1] This Journal, 19, 24: Smith's method: *Eng. Min. J.* (1900), pp. 307-364.

[2] *Eng. Min. J.* (1895), pp. 369 and 387.

[3] *Trans. A. I. M. E.*, July, 1897.

homogeneous material have been effectively sampled down to a small portion for a "battery test" by the method of repeated siftings with removal of pellets, as suggested for vein rock (I). Some of the larger mills send the concentrates to smelters in steel cars having a cross-section somewhat like an inverted hyperbola while the smaller concerns ship in oil barrels or casks.

To avoid rehandling, the concentrates of each grade are often sampled in the cars or other containers, just before weighing, by means of a pointed tube with a slit on the side, something on the principle of the cheese tryer. This instrument seems to drive back the water a little and produce a sample that is a little too dry, and therefore a little too rich in the red metal. As the percentage of moisture continually varies in all mill products, it is necessary in all comparative work to calculate assays to dry weights of material.

Principle of the Fire Assay.—The ideal would be attained, if one could succeed in melting and reducing all the copper in a sample by fifteen or twenty minutes' fusion in a pot-furnace, without carrying any iron into the button, to be incorrectly weighed as pure copper. In practice it is found that we can so flux and fire native copper concentrates (over 40 per cent. copper) that the loss of copper in the slag can be kept at about 0.25 per cent. (of the mineral weighed) and shall be balanced by iron in the copper button, equivalent to 0.25 per cent of the original sample. It is also possible to tell, by the eye, the purity of the copper button, and the waste in the slag, within a limiting error of about 0.1 per cent. either way.

With low grades of mineral and slags, the correctness of the assay can not be told so closely by the appearance of button and slag, but a button entirely free from iron can be distinguished from one carrying enough to affect the assay result 0.1 per cent. or more. Accordingly, some laboratories fire low grades (5 to 30 per cent. copper) with such a fluxing and reducing mixture that no iron shall be carried into the button. The copper lost in the slag (usually 0.3 to 0.4 per cent.) is quickly estimated with sufficient accuracy by calculating roughly the weight of slag produced (according to formulas to be given), crushing a portion, estimating copper by blue test, and adding the total weight of copper found in assay slag to the weight of the button.

Check assays should always agree on rich grades within 0.2 to 0.4 per cent., and on poor grades within 0.2 per cent. From month to month, the fire assay, when properly conducted at a smelter, should check the output of the reverberatories, adding the slight loss in the waste slag from the cupolas.

A large assay button from rich material should be bright on all sides and have a small hole in the top with wavy or rough upper surface surrounding the cavity. A very smooth button and red slag indicates undue slagging off. If the large button has no hole and is dark on the bottom, except possibly a slight ring or film of brown on the outer edge, it will be too high in iron. Small buttons from low grades should be bright, and smooth, or with striations on upper surface, but no cavity.

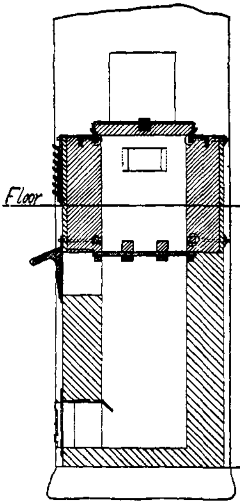
Pimples and pits, or a purple film on such a button are produced by sulphur, or by fragments of coal having dropped into the crucible. The slag from rich material (over 40 per cent. copper) should be colored black, or dark brown,—from low grades, black, or nearly so.

APPARATUS AND FUEL.

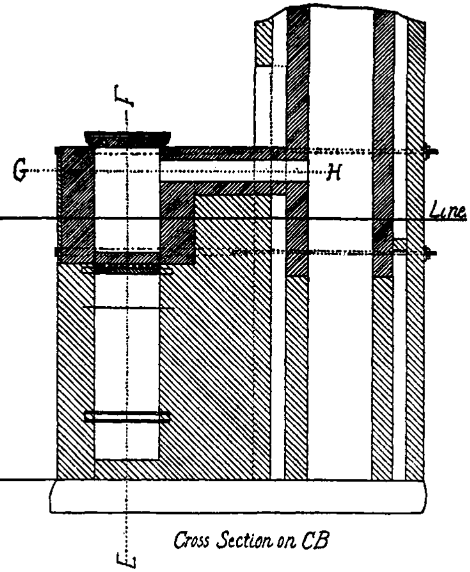
A pot furnace, similar to the accompanying illustration, is generally employed, but a much higher temperature and quicker heat is required than can be attained with coke and natural air-draft in twenty-minutes' time. To secure the quick, sharp heat, the furnace and stack must be brought to a high temperature before charging the crucibles, by egg-size soft coal and natural draft or by coke with an air-blast under the grate.

At the new laboratory of the C. and H. Stamp Mills, the blast produced by the smallest size Root blower is passed through a 2-inch galvanized iron pipe, to the air-tight ash-pit of the furnace. Two rows of fire-brick (2.5" × 2.5" cross-section) are placed across the grate, and the fuel is kept at least 2 inches above the top of these.

The mill of the Mass Mining Company is said to have installed a furnace pot heated with air-blast gasoline burners, which may be very satisfactory for a small plant. Rich grades melted in sand crucibles require a quick, sharp heat. Low-grade stuff, if fired in Denver clay crucibles, requires that the heat should be lowered to cherry-red just before charging, and that part of the soda be



Cross Section on EF.

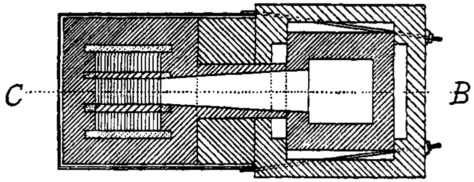


Cross Section on CB

Scale: 0.3" = 1 foot.

▧ Common Brick.

▨ Fire Brick.



Cross Section on GH.

placed on top of the charge in the crucible. These precautions are taken to prevent pellets sticking to the inside walls of the crucible.

Not only different classes of material, but the same grades, if fired in different makes and styles of crucibles, will require considerable changes in fluxes, especially in the reducing agent—cream of tartar. Crucibles of Denver clay, or of sand, affect the slag in a manner similar to the action of "basic," or "acid" linings in Bessemer converters. The more basic Denver crucible with round top and tightly fitting cover requires more flux and far less reducing agent, than an open-shaped triangular sand crucible. The latter is better to keep iron out of the large copper buttons from rich material, while the Denver clay with extra thin walls has proved better for low-grade silicious stuff.

THE ACTUAL ASSAY.

Fluxes.—The cream of tartar must be 99.5 to 100 per cent. pure, and all the chemicals must be free from sulphur or sulphates. For soda, it has been found advisable to buy the "Natrona brand" sodium bicarbonate, which is fused in a large iron ladle, poured into a smooth iron dish, or ladle, to cool, and then pulverized through a sieve of 20 meshes to the linear inch.

Refined crystallized borax is fused in a Dixon graphite crucible, poured into an iron dish and pulverized to pass a 20-mesh sieve. Powdered silica is occasionally employed for very ferruginous slags, such as blister slag, and powdered hematite (Fe_2O_3) for very silicious material, such as gravels, or carbonates and silicates of copper.

Weighing.—The moist material is dumped by the assayer on a sampling board about 15″ x 20″ in area. Operators formerly used a tray made of straight-grained wood, which has to be wet with water frequently and the superfluous moisture removed with a cloth. The best thing, in every way, that we have used is a vulcanite tray, 15″ x 19″ in size, such as is sold for photographic purposes. The long side of the tray next to the operator is cut out, and we have a sampling platform which does not absorb moisture, and does not break or wear out with months of use.

The assayer quickly mixes the sample with a large steel spatula, and covers up the pile which is then pushed outward from the center and flattened to a layer about 1 inch thick and 1 foot square, or a little more. With a steel spatula (8-inch blade), vertical slices are quickly taken at regular distances apart (generally from 9 equi-distant points), dipping to the tray each time in such a manner as to make up 1000 grains on the pan of the pulp balance. This first sample is put in a dish or can, to be dried for the estimation of water, and a second portion is immediately taken for a copper assay and placed on oiled or smooth white paper.

Mineral containing 70 to 95 per cent. copper makes so little slag of itself and needs so little flux, that there would not be enough from the gangue present, to cover the button and keep it deoxidized while cooling. On this account a large stock of old assay slag is accumulated, preferably from low grades, ground to pass a 20-mesh sieve, assayed for copper, and a certain quantity added to each crucible charge of rich material to act as a regulator and a cover for the button. If known grades, varying within narrow limits, are regularly assayed, a large quantity of complete fluxing mixture can be made up and added by measure instead of weight. Otherwise, weigh fluxes roughly, according to formulas determined by experience, mix with the spatula, transfer to crucibles and add a cover $^1/_{16}''$ to $^1/_8''$ deep of cream of tartar.

Scrape away the hot coals from the surface of the rows of brick in the furnace, close each crucible when in position, with a clay cover to keep out coal, poke the hot fuel around the crucibles, and fill in fresh coal (egg size) up to 1 inch below the top of the sand crucibles, or a little higher for Denver clay crucibles. The covers can be made in wooden molds from a mixture of fire-clay and ground fire-brick. Old crucible bottoms luted with clay could be employed. When using soft coal, the writer has the fire poked gently in from five to seven minutes from the start (according to the sharpness of the heat) coaled lightly in four minutes more, poked again five minutes later, and the assays taken out two to three minutes afterwards, the furnace having come to a very high heat —total time sixteen to eighteen minutes. Leave any charge not melted, until it just comes to quiet fusion. The melts should not be jarred while cooling. The success of the assay depends largely on the quick and sure regulation of the time and degree of heat.

The above manipulation is for soft coal and a double-walled tight furnace. Coke, or gasoline fuel, would require different manipulation to get the same results in the time allowed (in general not over twenty minutes for complete fusion). If low grades are to be fired in Denver "E" crucibles, the furnace and stack should be thoroughly heated, but the grate cooled down to a bright red by taking the furnace cover off for a few minutes just before firing the assays. The heat can be brought up within the time allowed, but the slower start helps to prevent pellets from sticking to the crucible.

Specimen charges are here given to show the average weights which each flux loses in melting down, and thus to indicate a method by which any one can approximately calculate what total slag will be produced in any case, and, in conjunction with the colorimetric assay of that slag, the total copper slagged away from the button.

Small No. 5 Hessian Triangular Crucibles.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Rich mill concentrates, sample = 1000 grains	(Cu + H_2O) = 88	120
70 to 50 grains sodium carbonate	40	42
70 to 50 grains borax glass	0	70
250 grains assay slag (0.3 per cent. copper)	0	250
300 grains cream of tartar	75	75
Total slag		557

Actual weight of slag found to be 550 to 570 + grains.

Small No. 5 Hessian Triangular Crucibles.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Poor (slime) mineral, 1000 grains	(Cu + H_2O) = 33	670
150 to 200 grains sodium carbonate	40	90
150 to 200 grains borax glass	0	150
350 grains cream of tartar	75	88
Total slag		998

Actual weight varies from 1000 to 1025 grains.

As the only appreciable impurity of copper assay buttons is metallic iron, if we desire an exact assay on any unknown sample, we have only to determine the iron in the button and the trace of copper lost in the slag, calculate both results to the 1000 grains of mineral tested, and apply the corrections to the weight of the button. This calculation will furnish also a guide as to the effects of experimental variation of fluxes and conditions of heat.

Specimen charges employed in practice at lake refineries are presented in the following table. They are based on the original paper of Mr. M. B. Patch and on the later experience of the writer and assistants with a variety of material.

It will be advisable to use the higher limiting quantity of soda on rich concentrates, when the old assay slag employed has been preserved from 1000 grain assays of low-grade material only, as such slag is proportionately lower in soda and oxide of iron than the usual slag produced years ago. Conglomerate mineral contains much more ferric and titanic oxides than the amygdaloid. In all cases there is some fine metallic iron in mill products, due to the wearing of the stamps.

COMPOSITION OF FLUXES.

Class of material.	Source.	Usual limits of Cu.	Limiting per cent. of water.	Make of crucible.	Weight of sample. Grains.	Fluxes—all weights in grains.						Time in minutes.
						Cream of tartar.	Fused soda (Na_2CO_3).	Borax glass.	Old assay slag.	Iron ore (Fe_2O_3).	Sand (SiO_2).	
[1]Mill products, rich concentrates.	Conglomerate.	90–70	1–5	H or B	1000	300	50–150	50	250			15–17
[2]As above only much coarser.	Amygdaloid.	95–75	0.5–3	H or B	1000	300	150	50–40	250			16–18
				Denver "G"	2000	300	250	100	350-375			17
Medium grades.	Conglom. or amygdaloid.	70–40	5–10	H or B	1000	300	100–150	100–150			0–100	
[3]Lean grades, table stuff, etc.	Conglomerate.	30–10	10–20	B or H	1000	300–350	150–250	200		0–50		16–18
				B or H	500	300	150–200	150–200				17
				D	1000	200	150 on top of charge. 200 mixed in.	300		0–50		16–17
[3]Lean grades, table stuff, etc.	Amygdaloid.	30–10	10–20	B or H	1000	300	200–250	200		50		16–20
				D	1000	200	150 on top. 225 mixed in.	375		0–50		16–18
[4]Reverberatory slags.	From mill concentrates.	25–10	0	B or H	500	300	200	200				18–20
				B or H	1000	400–450	320	320				20
				D	1000	350	400	400				16–20
[4]Reverberatory slags.	From melting rock, barrel work.	25–10	0	B or H	500	350	200	200		100		16–20
				B or H	1000	450	350	350		200		18–20
				D	1000	360	400	400		200		16–20
Blister furnace slag.				B or H	1000	300–400	300	300			150	17–20
Lean gravels and silicious ore.		5–10		D	1000	350+	400	400		50–100		17–20
Copper and iron oxides.	Surface ores, no sulphur.			H or B	1000	350–400	300	350			50–150	17–20

B = U Battersea Δ-shaped top.
H = Small 5 Hessian Δ-shaped top.
D = "E" special thin wall, Denver clay, O shape.

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[1] Quick heat. Increase cream of tartar for black oxidized stuff.

[2] Best assay for very coarse Cu.

[3] Low grades average more silicious than years ago.

[4] [illegible] mesh sieve. Coarse shot picked out and weighed separately.

It is evident, from the foregoing description, that the Lake Superior fire assay bears no relation to the empirical matting assay in use at Swansea, but is a practical method, easily controlled when once thoroughly learned, and sufficiently accurate for all technical purposes.

NOTES ON THE ESTIMATION OF COPPER BY POTASSIUM PERMANGANATE.

By H. A. Guess.

Received April 25, 1902.

Although at various times, during the past few years, different chemists have proposed the use of an alkaline thiocyanate as a precipitant in the estimation of copper,[1] and although the results have been shown to be sufficiently accurate for technical purposes, the fact remains, that the method has made little headway, in competition with the electrolytic, cyanide, or iodide methods, in technical work, particularly in the metallurgical laboratories of the West, where the iodide method is greatly in favor.

In the iodide method, as generally practiced, the copper is first precipitated by aluminum strips, and while this precipitation is fairly rapid and complete in concentrated solutions, it is not at all so in dilute solutions of 20 milligrams or less of copper in a bulk of 150 cc. of dilute sulphuric acid. Furthermore, other metals, particularly arsenic, interfere by being precipitated along with the copper, and have to be rendered inert by oxidation with potassium chlorate. On the other hand the precipitation of copper as thiocyanate is practically complete at the moment of adding the precipitant; no other metals interfere, silver being the only other metal precipitated by an alkaline thiocyanate from an acid solution, and its thiocyanate is unacted upon by the subsequent caustic alkali treatment.

It has seemed to the writer that the main drawback to the method as so far proposed is the use of asbestos as the filtering medium, and the consequent necessity of filtering-pumps, which in a laboratory doing 100 or more copper assays in a day would render the process awkward and cumbersome. For the past six

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[1] This Journal, **20**, 610; **22**, 685, *et seq*; *Am. J. Sci.*, **163**, 20-26; *Chem. Centrbl.*, **1**, (19), 1085 (1899).