

Journal of the Society of Chemical Industry.

No. 10, Vol. XXXII.

MAY 31, 1913.

No. 10, Vol. XXXII.

London Section.

Meeting held at Burlington House, on Monday, 5th May, 1913.

PROF. W. R. E. HODGKINSON IN THE CHAIR.

ORE DEPOSITS OF HU-NAN AND HU-PEH.

BY W. R. SCHOELLER.

These two provinces of Central China are situated the former to the south, the latter to the north, of Tung-ting lake (Tung-tung hu), as indicated by their names. (Hu-nan: South of the Lake; Hu-peh: North of the Lake.)

The following description of the mineral deposits of the two provinces includes nearly all those that have come under my notice, and while many more are still awaiting discovery this list is, I believe, the most complete yet published, and may help to give an idea of the vastness of the natural resources of the country. All the analytical data quoted are original; some have been obtained by the examination of specimens, while in the case of stibnite, galena, realgar, and mixed sulphides the figures represent the composition of large quantities of ore, sometimes exceeding five hundred tons.

Foreigners are not permitted to acquire mining rights in China, nor are they allowed to reside outside treaty ports; it is even difficult to secure a passport enabling them to visit the country districts. The opposition of the Government and the intense anti-foreign feeling will probably delay the development of the mining industry for a long time to come. With a few exceptions, the Chinese refuse to accept European guidance in their industrial enterprises, though attempts to do without it have always resulted in failure. China is thus a store-house of mineral wealth available for the future.

As regards means of communication in the two provinces, the Hankow-Peking railway carries no ore, as there are no mines along the line; the colliery railway from Ping-hiang to the Siang river brings down coal and coke for transshipment into lighters. All other transport is done by water, and full advantage is taken of the natural waterways. Hankow can be reached by large ocean-going vessels for 7-8 months in the year (April-November). Shallow-draught river steamers, chiefly British and Japanese, ply between the following ports:—

- 1° Shanghai—Hankow. All the year round.
- 2° Hankow—Ichang. All the year round.
- 3° Hankow—Siang-tan. April—November.
- 4° Hankow—Chang-te. May—November.

In addition to these steamers, innumerable junks trade on all rivers down to the smallest creek. Above Ichang, the Yang-tze winds its way through some hundred miles of narrow gorges, and navigation becomes impossible except for specially constructed craft, owing to dangerous rapids.

For the description of the various ore deposits, it will be convenient to group them under several heads.

Antimony ores of Central Hu-nan.

The Siang-kiang would appear to form the eastern boundary of the antimony belt. The district situated between that river and the Yuen-kiang and of which the city of Sin-hoa may be said to be the centre, produces the purest and richest stibnite ore, a typical ore assaying 57.04 per cent. Sb, and 0.127 per cent. As, with traces Pb and Cu. However, the arsenic is usually well below 0.1 per cent. The gangue amounts to about 15 per cent, and consists of quartz, occasionally mixed with schistose rock. The mineral is most frequently coarse-crystalline,

showing long stout prisms, of strong lustre. Massive stibnite is not uncommon, and the richest ores are of this variety, with an antimony content of 60 to 65 per cent.

With the exception of one or two mines owned by the Hua-Chang Co. of Chang-sha, there are no mines in the European sense of the term. The workings are merely man-holes made in the mountainside; as soon as a certain depth is reached, ground water or the want of ventilation make work impossible, and another hole is dug near by. In this manner only the surface of the ore body is scratched. The miners sell the ore by the picul to local dealers, who send it to the nearest river, whence it reaches Chang-sha or Yi-yang. At both these places the ore is liquated for crude antimony, while regulus is also made at Chang-sha and Han-yang. The liquation residues, containing 20-30 per cent. of metal, have accumulated since smelting began, but are being used of late in the manufacture of regulus by the volatilisation process. The antimony sulphide in the residues coating the gangue and forming a glaze after solidification, it is not possible to concentrate them by mechanical means, as the brittle sulphide slimes after crushing. The slimes from a 27 per cent. residue assayed 56.4 per cent.

To the north of the Sin-hoa district the deposits become poorer: near An-hoa there occur ores averaging 48 per cent. Sb, with 0.06 per cent. As and negligible quantities of lead, copper, and zinc. They are of granular texture and present a dull lead-grey appearance.

Low-grade ores are also known to occur. A 25 per cent. ore showed beautiful isolated crystals several inches long embedded in a slaty gangue. Another ore (28.94 per cent. Sb) of extraordinary hardness consisted of an intimate mixture of quartz and stibnite in fine-grained masses. Both ores were practically free from arsenic.

Passing into S.W. Hu-peh the ore deposits show an increased proportion of arsenic, a sample giving 51.75 per cent. Sb and 0.43 per cent. As.

The same may be said of stibnite and crude from the province of Kweichow, some of which finds its way down the Yuen-kiang. Specimens were examined with the following results:—

- 1° Ore. Sb 62.99%—As 0.846%—Pb 0.18%—Cu, Zn: traces.
- 2° Crude. Sb 69.85%—As 0.46%
- 3° Crude. As 0.303%

The export of stibnite and crude antimony dates back about eight years when the inflated price of the metal made mining very profitable.*

The "Mineral Industry," vol. XX. (1912), p. 45, mentions that China is first in the production of antimony; and that the ore comes from a number of places to the north-west of Tung-ting lake. South-west is more correct. The same year-book also states that "at Hankow, Carlowitz and Co. are engaged in the smelting of antimony and lead." No smelting was in progress at Hankow at the time the book was written. (For additional information concerning antimony ores, see this Journal, 1913, p. 260.)

Lead-zinc sulphide deposits of Southern Hu-nan.

Deposits of this kind abound in the southernmost part of the province, between the Kwang-tung boundary and Heng-chow. In the neighbourhood of that city some non-argentiferous galena is mined which, as is frequently the case with ore of this description, is almost free from other metals: Pb 74.7 per cent.; Zn 1.5 per cent. Farther south, near Cheng, are found deposits of complex sulphides. These ores are intimate mixtures of galena, blende and pyrites carrying silver. A mine sample gave the following figures:—Pb, 10.7 per cent. Zn, 11.4 per cent.; Fe, 23.2 per cent.; Ag, 9.8 oz. per ton of 2240 lb.

No mining is done in this locality, though the presence of old workings and slag dumps show that the deposits

* Mining Journal, Sept. 15th, 1906, p. 305; June 11th, 1910, p. 740.

were worked at some former period. Examination of a specimen of slag proved it to be a ferrous silicate free from lime containing $\frac{1}{2}$ per cent. of lead and 5 oz. of silver.

The important Sui-ku-shan mine worked by the Hu-nan Board of Mines is the only one in the district in active operation. The ore is argentiferous galena associated with blende, pyrites and calcite. Where the blende predominates, the ores become auriferous. Their composition is shown in the following table, A—C:—

Constituents.	A	B	C	D
	Galena.	Blende.	Mixed.	Lead Concentrates.
oz. per (Silver. long ton. (Gold..	28.74 nil	11.21 0.16	12.60 0.01	37.11 nil
Lead	59.56	12.60	23.05	76.97
Silver + gold ..	0.08	0.04	0.01	0.12
Arsenic	0.11	0.60	0.25	0.04
Antimony	0.22	0.24	0.46	0.22
Copper	0.76	1.02	2.42	0.20
Bismuth	0.41	0.03	0.04	0.03
Iron	1.44	9.97	6.03	1.30
Alumina	1.28	1.64	1.80	0.80
Manganese	1.27	0.36	0.49	0.06
Zinc	12.00	39.00	24.34	2.33
Lime	1.10	nil	3.40	nil
Magnesia	0.33	nil	0.39	nil
Insol. gangue ..	4.47	4.02	12.70	0.95
Barium sulph. ..	nil	nil	nil	nil
Sulphur	17.25	29.99	22.16	15.46
CO ₂ and loss....	0.22	—	2.43	1.47
	100.00	100.18	100.00	100.00

A considerable proportion of the ore mined is dressed at the mine, giving lead concentrates the composition of which is also given in the table under D. The total annual production is about 8000 tons, that of lead concentrates 3000 tons. The latter is chiefly exported to Germany, also to Japan and the United Kingdom. The blende and mixed sulphides are sold to a German firm having an ore dressing plant at Woo-chang where the material is further separated previous to exporting.

Some of the galena produced at Sui-ku-shan is sufficiently pure to be shipped without previous separation. The difference in quality between this class of ore and the lead concentrates is shown by the following assays:—

Concentrates: Silver 40.9 oz.; Lead 74.36 per cent.; Zinc 3.05 per cent.
Undressed lumps: Silver 32.4 oz.; Lead 64.35 per cent.; Zinc 7.55 per cent.

Spelter is also made at the mine after native processes by reducing the ore in small pots, the zinc condensing inside the cup-shaped cover. Half the zinc present in the ore is lost in the operation, but the spelter is remarkably pure, containing 99.56 per cent. Zn, 0.20 per cent. Pb, 0.18 per cent. Fe.

The Chinese extract silver from galena, though they do not appear to suspect the presence of noble metals in copper ores. The lead ore mixed with coal is subjected to an oxidising roast in stall-like furnaces, blast being supplied by bellows. Part of the lead is volatilised, and the fused litharge runs off the surface of the metal until the pure silver remains. All the lead is lost.

A modern blast-furnace plant was erected by the Hu-nan Board of Mines at Chang-sha for reducing Sui-ku-shan galena. After a few months' run in 1910 the American staff was discharged. Difficulties arose in smelting, and the plant being unable to cope with the ore was shut down.

The Realgar deposits of Northern Hu-nan.

A deposit of very pure realgar of considerable magnitude occurs near Li, Northern Hu-nan. The ore is crystalline and of a beautiful red colour. As mined, it

averages 95 per cent. of arsenic bisulphide, the following analysis showing its composition:—

Arsenic	66.60
Sulphur	28.56
Al. silicate	1.78
Organ. matter	0.42
Carb. of lime	0.93
Carb. of magnesia	0.50
Iron	0.22
Zinc	0.10
	99.11

Sb, Cu, Pb: nil.

The Chinese use realgar in moderate amount for agricultural and medicinal purposes, but are unwilling to export it in large quantities as it commands a higher price at home.

An arsenic plant was put up at Han-yang for the manufacture of arsenious oxide. After a few unsuccessful trials, plant and machinery were left to their fate.

Miscellaneous deposits of Hu-nan.

A rich gold mine situated between Chang-sha and An-hoa is being worked at the present time. The ore, which is quartz carrying pyrites and visible gold, is milled and then washed, but the tailings are by no means free from gold. A wooden cradle is used in Hu-nan for washing ores. The operator works it floating on water, in which he stands up to his knees. It may here be mentioned that Hu-nan antimony ore is free from, or very poor in, gold.

Some mixed lead-zinc sulphide deposits occur in North-Eastern Hu-nan, also a very dark blende free from lead. A specimen assayed 49.6 per cent. Zn, 4.8 per cent. Fe, 0.28 per cent. As.

Pyrolusite (46.0 per cent. Mn) and pyrites (49.74 per cent. S; Cu nil; large well-developed pentagondodecahedra) are found along the Siang-kiang, and an oxidised copper ore assaying 40 per cent. on the Yuen-kiang.

I have no precise information as to the locality of these deposits. Very probably some stream-tin is washed in Hu-nan itself, on the Kwang-si border.* A specimen of sand-grain size was found to contain 72.10 per cent. tin.

Copper deposits of Hu-peh.

A few miles N.W. of Ching-kuo (Eastern Hu-peh) there extends a short and narrow valley between rocky hills, the sides of which present numerous outcrops of copper-bearing veins, some of which show patches of gossan brightly coloured with carbonates of copper. The surface deposits show all the effects of leaching and

Constituents.	Vein (A).	Gossan (B)
Total copper	36.19%	20.78%
oz. per Silver	16.07	1.90
ton Gold	0.26	nil
	per cent.	per cent.
Insol. gangue	30.30	20.30
Sulphur	8.55	0.52
Copper oxide	11.02	37.22
Ferrie oxide	3.04	12.55
Copper as sulphide	26.80	—
Iron as sulphide	4.18	—
Sol. alumina	4.15	4.20
Lime	0.81	5.62
Magnesia	0.09	0.54
Lead	0.02	trace
Bismuth	0.06	0.01
Arsenic, antimony	nil	nil
Zinc	nil	0.30
Nickel	nil	0.24
Carb. acid, oxygen, etc.	9.33*	19.34†
	100.00	100.74

* By difference.

† Loss on ignition.

weathering, and rich sulphides predominate. Thus one vein showed a core of chalcopyrite surrounded by chalcocite which in its turn was coated with malachite, in a casing of clayey material. The analysis given under A

* Compare Mining Journal, April 10th, 1913, p. 377.

represents the composition of the vein-stuff; that under B, a sample of soft, porous, hand-picked gossan. In other places, amorphous hematite accompanies the sulphides, while magnetite has been found in at least one place; the material contained: Cu 7.6 per cent.; Fe_2O_3 31 per cent.; Fe_3O_4 28 per cent.

Other varieties of ore from the same district are cuprififerous pyrites (1 per cent. Cu) and complex sulphides, a specimen showing 8.8 per cent. Cu, 5 per cent. Zn, and nearly as much lead. All these ores contain silver and generally gold. The maximum amounts observed were 1.09 oz. Au and 26.9 oz. Ag. per ton of 2240 lb.

The deposits have been worked in the past, but nothing is done at present. The place is of easy access, coal and metamorphic limestone are plentiful in the neighbourhood, while the river is quite near; but the villagers of the valley are fiercely anti-foreign, and oppose the intrusion of any outsiders, even Chinese. However, small quantities of ore are smelted locally by heating a few pounds at a time in pots, when the oxide and sulphide of copper react on one another. The metal so obtained is made into tools and various implements.

Not far from the spot where the Hankow-Peking railway crosses the mountain range along the N.E. border of Hu-peh, cuprififerous pyrites is met with. Specimens assayed 4 per cent. Cu and 1 oz. of gold per ton. Nothing has yet been done in that district.

A unique native copper ore occurs near Choo-shan, N.W. Hu-peh, in what is said to be a most inaccessible spot in the mountains. I had a specimen weighing 80 lbs.; its colour was almost pure white except for the short thick ramifications of metallic copper visible on the surface. When treated with dilute hydrochloric acid, the entire non-metallic part which consists of calcite containing some soluble copper dissolves, leaving a sponge-like skeleton of metal:—Native copper, 65.8 per cent.; Soluble CuO , 4.1 per cent.; CaCO_3 , by difference 30.1 per cent.

Miscellaneous deposits of Hu-peh.

Complex sulphide ores are found near Foo-chih, on the border of Kiang-si province. Metals were found to be present in the following proportions:—Pb, 23.4 per cent.; Cu, 2.0 per cent.; Zn, 19.3 per cent.; As, 1.08 per cent.; Sb, nil.

A specimen of galena from the district S.W. of I-chang assayed 66.8 per cent. Pb and 36.9 oz. Ag. The eastern and western parts of the province south of the Yang-tze are almost certain to abound in mineral deposits, though little is known concerning them.

Coal and Iron.

In conclusion I will briefly mention the occurrence of coal and iron ore. Anthracite and bituminous coal are plentiful in Hu-nan, and numerous small mines have been worked for a long time by the natives. Specular iron is also found.

An important colliery is in operation at Wong-tsze-kong, near Ta-yeh. Here is also found a mountain of iron ore which is quarried and smelted in the Han-yang Iron and Steel Works; the coke used in smelting is derived from the coal mined at the Ping-hsiang Colliery which although situated in Kiang-si province is only accessible from Hu-nan.

The Ta-yeh iron mine, the Ping-hsiang colliery, and the Han-yang smelting works are under one management, assisted by a European staff. A more detailed description of this important concern will be found in the "Mining Journal," October 8th, 1910, Supplement, p. iv.

Meeting held at Burlington House on Monday, 5th May, 1913.

MR. W. F. REID IN THE CHAIR.

SOME REACTIONS OF HYDRAZINE NITRATE.

BY W. R. E. HODGKINSON.

About 1902 a series of experiments was commenced to overcome a difficulty in connection with the employment of copper driving-bands on gun projectiles and the cupro-nickel envelope of bullets for rifled small arms. Guns

especially become fouled on parts of the rifling of the bore—coated with copper—which may increase to an extent sufficient to interfere with accurate shooting and may have serious effects on the gun.

In these early experiments, guided by theory, a solvent for copper and nickel but inactive towards iron, was sought for. Ammonia in the presence of air suggested itself, but an ammoniacal solution of an amide—formamide or the like—seemed likely to be and proved a better solvent than ammonia alone, but also depended on its action either on the absorption of atmospheric oxygen or on the presence of a small amount of a carrier such as cuprous chloride. Quicker effects were obtained by the use of some oxy-salts, as nitrate, permanganate, persulphate, chromate, some peroxides, picric acid, or nitrophenol in conjunction with the ammoniacal solution of the amide. Practically any amide, if soluble enough, can act as a solvent of copper under these circumstances.

As the activity of these oxy-salt solutions ceases with the exhaustion of the oxy-salt, an electrolytic process was devised in which an ammoniacal amide solution was the electrolyte, and later it was found that an ammonium salt of certain organic acids might be used in the presence of excess of ammonia and the complete absence of halogens, alkalis, and some other substances as solvent for copper and nickel but completely without action on iron.

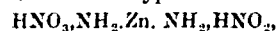
In the course of these experiments it was noticed that ammonium nitrate in water solution and also in a melted state exerted a strongly solvent action on a number of metals. Zinc, cadmium, magnesium—in this order—were found to dissolve with moderate rapidity in a cold (10° – 16° C.) nearly saturated solution of ammonium nitrate with scarcely any gas evolution. Iron, aluminium, lead, tin, bismuth, silver, and mercury showed no or very little action after days of contact. Copper, nickel, cobalt, and some of their alloys were slowly attacked during the same time.

Ammonium nitrate in the melted state at a temperature of about 160° – 165° reacted with zinc, cadmium, copper, cobalt, and nickel, and the reaction became violent if the metal was in a fine state of division or the temperature rose 10° or 20° above the melting-point.

Whether in the melted state or in solution the first stage of the reaction consists in the liberation of a small amount of ammonia.

The next stage is possibly the displacement of nitric hydrogen which is then taken up by adjacent molecules of nitrate, resulting in the formation of some nitrite. A third stage, produced by heating the solution of nitrate with the metal, is the reaction between the nitrite so produced and the ammonia of the original salt, that is, the evolution of nitrogen. This might also be due to the decomposition of ammonium nitrite by the heating.

The final products in solution when the substances were not heated consisted of nitrite of the metal as well as nitrate and excess of ammonia salt unacted upon. Possibly a double salt of the type



is produced.

Analyses of these products showed that approximately the acidic portion was half nitric and half nitrous. It was very difficult to obtain anything like a pure salt by recrystallisation, either from alcohol, acetone or water.

All the compounds obtained by the action of metals on the aqueous solution of ammonium nitrate rapidly absorbed CO_2 from the air. This was especially noticeable in the case of the zinc and cadmium products.

A strongly ammoniacal solution of ammonium nitrate has been used for the evaluation of galvanised iron from which all the zinc is dissolved, that in the facing layer and that in the zinc iron alloy; the alloyed-iron being converted on air contact or by later addition of a persulphate, into ferric hydroxide.

Nitrates of bases as aniline, toluidine, behave both in solution and when fused with most of the metals mentioned, but more especially with zinc, in a manner perfectly analogous to ammonium nitrate.

With *p*-toluidine nitrate and zinc, there were produced toluene, ore-ol, zinc nitrate, and very little tarry