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VANCOUVER 5, B. C. CANADA

MEMORANDUM

TO: Distribution DATE: July 12, 1971.
FROM: K. M. Dawson FILE: Gib.9-2 and Gib.10-1.
RE: Gibraltar Copper Oxide Mineralogical Study

SUMMARY

1. Twenty Gibraltar pulps were submitted for comparison assay. Placer Labs oxide and total copper assays are 37% and 8% higher, respectively, than Chemex assays. Comparison between Placer, Loring and Crest Labs shows Placer oxide assays to be 16% higher than Loring and 29% higher than Crest. Total copper assays are nearly identical.
2. Mineralogical study of ten pulps show the average composition of the copper mineral fraction to be: chalcocite 42%, chalcopyrite + bornite 24%, cuprite 20%, malachite 9% and native copper 5%.
3. Leaching the pulps showed that the copper "oxide" minerals cuprite and malachite contribute the bulk of the oxide assay, but other copper minerals, particularly chalcocite, contribute significantly.
4. Data from controlled leaching of pure mineral specimens allows calculation of proportional contributions of each copper mineral to the oxide assay: cuprite 55%, malachite 31%, chalcocite 11%, chalcopyrite + bornite 2%, native copper .5%.
5. Assay overrun due to copper sulfides compensates for assay shortfall due to incomplete solution of cuprite. The net result is the Placer oxide assay is about 5% less than the ideal figure. Chemex, Loring and Crest labs would be about 25%-40% below the theoretical oxide content.

INTRODUCTION

The purpose of this study is to determine the identity and relative amounts of copper minerals contributing to Gibraltar copper oxide assays. This information will assist in the evaluation of the abundance, distribution and potential recoverability of copper oxide minerals.

Twenty drill core pulps showing a range of copper oxide assays were selected for study. A split of the pulps was sent to Chemex Labs for duplicate copper oxide-total copper assay. The remaining pulps were separated on the Superpanner, and the mineralogy of both the heavy fractions and tails was determined under the binocular microscope.

Ten heavy fractions were submitted to an oxide assay leach (30% H₂SO₄)

for 90 minutes) and re-examined. The amounts of copper minerals were visually estimated before and after leaching.

A controlled leaching experiment was run on pure specimens of chalcopyrite, chalcocite, cuprite and native copper. To duplicate the oxide assay extractions of Chemex and Placer labs, weighed mineral specimens were leached in both 5% and 30% H₂SO₄ for varying times, the insoluble residues re-weighed and the Cu content of the solutions determined by atomic absorption.

1. Comparison Assay

Of the 20 pulps selected for study, 10 were examined in detail and re-assayed by Chemex Labs. A comparison between Placer and Chemex assays is given in Table 1.

Chemex copper oxide assay involves a 30-minute leach in 5% H₂SO₄, then AA analysis of filtrate. Chemex total assay involves heating 2 grams of sample in 25 ml. of 70% perchloric acid + 5 ml. concentrated HNO₃ to 203°C for 1½-2 hours.

Placer copper oxide assay involves a 90-minute leach in 30% H₂SO₄. Placer total copper assay is the same as that of Chemex. Some of the Gibraltar total copper assays were done by Loring Labs, using the same technique.

TABLE 1

Comparison of Placer and Chemex Copper Assays

Assay Tag No.	Placer (30% H ₂ SO ₄ , 90 min.)		Chemex (5% H ₂ SO ₄ , 30 min.)		Placer % Difference	
	Cu oxide	Cu Total	Cu oxide	Cu Total	Cu oxide	Cu Total
4831	0.882%	2.18%	0.59%	2.02%	+50%	+ 7%
4832	0.396	1.17	0.23	1.10	+42	+ 6
8684	0.194	0.25	0.13	0.22	+33	+12
8685	0.17	0.20	0.12	0.19	+30	+ 5
8686	0.44	0.48	0.36	0.45	+ 9	+ 6
8690	0.106	1.28	0.05	1.12	+53	+12
9631	0.112	0.21	0.06	0.22	+46	- 5
10311	0.196	1.19	0.13	1.11	+34	+ 7
10316	0.174	0.77	0.11	0.74	+37	+ 4
12010	0.164	0.51	0.11	0.37	+33	+27
					+37%	+ 8%
					Avg.	Avg.

It is notable that Placer copper oxide assays are significantly higher than those from Chemex Labs, the average difference being +37%. The percent difference between Placer and Chemex assays bears no apparent correlation to the magnitude of oxide and/or total copper assays, or to oxide/total assay ratios. The difference between Placer and Chemex total copper assays is relatively small and consistent, indicating some minor systematic difference in assay method may exist. A similar assay comparison was made by Brian Robson at Placer Labs. Three splits of each of 19 pulps were assayed by Placer, Loring Labs and Crest Labs. The results are given in Appendix. The average Placer oxide assay is .051% Cu, the average Loring oxide assay is 0.043% and Crest is 0.036%. Placer's oxide assay is about 16% higher than Loring's and 29% higher than Crest's. The oxide assay techniques of these two labs have not been studied. The total copper assays of all these labs are remarkably similar. Significantly higher Placer oxide assays in conjunction with similar total assays indicate that Placer's more rigorous oxide leach has liberated more copper by attacking a larger portion of the copper oxide minerals present, and/or by attacking copper sulfides and other copper minerals to a greater degree. The Placer oxide assay may be dependent upon the type and relative abundance of various non-oxide copper minerals present. To test these alternatives, two simple leaching experiments were run, as described below.

2. Mineralogy of Superpanned Pulps

Specimens from Superpanner concentrates and tails were immersed in water in a watch glass and examined under the binocular microscope in both reflected and transmitted light.

The Superpanner tails contain less than 2% copper minerals, mainly as very fine-grained chalcopyrite and chalcocite. Traces of copper carbonates and cuprite are present. A satisfactorily clean separation was obtained.

Under the binocular microscope, the ten Superpanner concentrates show the following average copper mineral content, recalculated to 100%:

Chalcocite	42%
Chalcopyrite	22
Cuprite	20
Malachite	9
Native Copper	5
Bornite	2

These figures give an approximate relative abundance of copper minerals in Gibraltar oxide ore.

Notable is the relatively low average malachite content and, referring to Table 2, its disproportionate effect upon Cu oxide assays.

Cuprite probably is more abundant than previously believed. Cuprite grains may be misidentified in reflected light, but are readily recognized when immersed in water or oil by their deep red colour in transmitted light.

Native copper may be partially oxidized or coated with limonitic minerals, hence not readily recognized. Native copper is fresher and

highly visible after leaching in H₂SO₄.

3. Mineralogical Composition of Pulps after Leaching

The ten selected pulps were subject to a standard Placer copper oxide assay leach, i.e. a 90-minute leach in 30% H₂SO₄. Specimens were re-examined under the binocular microscope, and mineralogical changes were noted. Table 2 summarizes changes in mineralogical composition:-

TABLE 2

Mineralogical Composition of Pulps Before and After Leaching

(est.% of total copper minerals before leach)
(est.% of total copper minerals after 30%
H₂SO₄, 90 min. leach)

Assay Tag No.	Oxide/Total (ratio)	Malachite (+ azurite)	Cuprite	Chalcocite	Chalcopyrite (+ bornite)	Native Copper
4831	.882/2.18 (.40)	$\frac{0}{0}$	$\frac{25}{10}$	$\frac{50}{60}$	$\frac{20}{20}$	$\frac{5}{10}$
4832	.396/1.17 (.34)	$\frac{0}{0}$	$\frac{20}{10}$	$\frac{35}{50}$	$\frac{20}{20}$	$\frac{25}{20}$
8684	.194/.25 (.78)	$\frac{20}{0}$	$\frac{30}{5}$	$\frac{30}{60}$	$\frac{15}{30}$	$\frac{5}{5}$
8685	.17/.20 (.85)	$\frac{10}{0}$	$\frac{30}{10}$	$\frac{40}{60}$	$\frac{10}{15}$	$\frac{10}{15}$
8686	.44/.48 (.92)	$\frac{50}{0}$	$\frac{40}{10}$	$\frac{10}{90}$	$\frac{0}{0}$	$\frac{tr}{tr}$
8690	.106/1.28 (.08)	$\frac{0}{0}$	$\frac{2}{0}$	$\frac{50}{50}$	$\frac{48}{50}$	$\frac{0}{0}$
9631	.112/.21 (.53)	$\frac{10}{0}$	$\frac{10}{0}$	$\frac{40}{50}$	$\frac{35}{40}$	$\frac{5}{10}$
10311	.196/1.19 (.16)	$\frac{0}{0}$	$\frac{tr}{0}$	$\frac{60}{60}$	$\frac{40}{40}$	$\frac{0}{0}$
10316	.174/.77 (.23)	$\frac{0}{0}$	$\frac{20}{10}$	$\frac{50}{60}$	$\frac{30}{30}$	$\frac{0}{0}$
12010	.164/.51 (.32)	$\frac{0}{0}$	$\frac{20}{5}$	$\frac{60}{70}$	$\frac{20}{25}$	$\frac{tr}{tr}$

Abundance of the various minerals listed is expressed as percentage of total copper mineral fraction of that sample before and after leaching.

The four specimens that contained the copper carbonates, malachite and minor azurite, all showed complete solution of these minerals under H₂SO₄ leaching.

Cuprite was present in all specimens tested. On the average, 65% of the contained cuprite was dissolved under acid leaching. Only small, corroded remnants of cuprite grains remain in the leached specimens.

Chalcocite, the most abundant copper mineral in oxide ore specimens, is attacked by the H_2SO_4 leach. Chalcocite grains are corroded, pitted and tarnished a deep peacock blue. Chalcocite, however, is weakly attacked relative to oxides and carbonates, with an estimated 5 to 10% of the mineral going into solution.

Chalcopyrite is only weakly attacked by H_2SO_4 . The mineral grains are not extensively pitted or corroded, and show an irridescent red-purple tarnish. Estimated solution of chalcopyrite is 3 to 5%. Chalcopyrite and bornite could not be distinguished in leached material.

Native copper is present in significant amounts in half of the tested specimens. The effect of acid leaching is weak corrosion and removal of oxide and limonitic coatings. Estimated solution of native copper is 1-2%.

The average copper mineral content of leached pulps, recalculated to 100% is:

Chalcocite	61%
Chalcopyrite + Bornite	27
Cuprite	6
Native Copper	6
Malachite	0

The change in mineral composition of pulps before and after leaching is depicted in a bar chart in Fig.1. The sulfide mineral content appears to increase after leaching, but this is only relative to the total copper mineral content which, by necessity, shows a net overall decrease.

Two important conclusions may be drawn from this experiment. Firstly, as expected, the copper "oxide" minerals (malachite, azurite, cuprite) contribute the bulk of the oxide assay. However, only two-thirds of the contained cuprite is dissolved by 30% H_2SO_4 . Secondly, the copper sulfides and native copper also contribute significantly to the oxide assay.

4. Controlled Copper Mineral Leach Experiment

Results of the above tests indicate that Placer's oxide assay technique may yield high results, and that "non-oxide" copper minerals may contribute significantly to the oxide assay. Changes in mineralogical content of pulps after leaching were estimated visually, and quantitative results could not be obtained. A more precise determination was needed of the amounts of copper minerals contributing to copper oxide assays. To this end a controlled leaching experiment was devised which would duplicate the effect of assay-leaching upon each of the Gibraltar copper minerals under differing leach times, acid strengths and sample grain sizes. Experimental procedure, as carried out by Brian Robson at Placer Research Center, is outlined below.

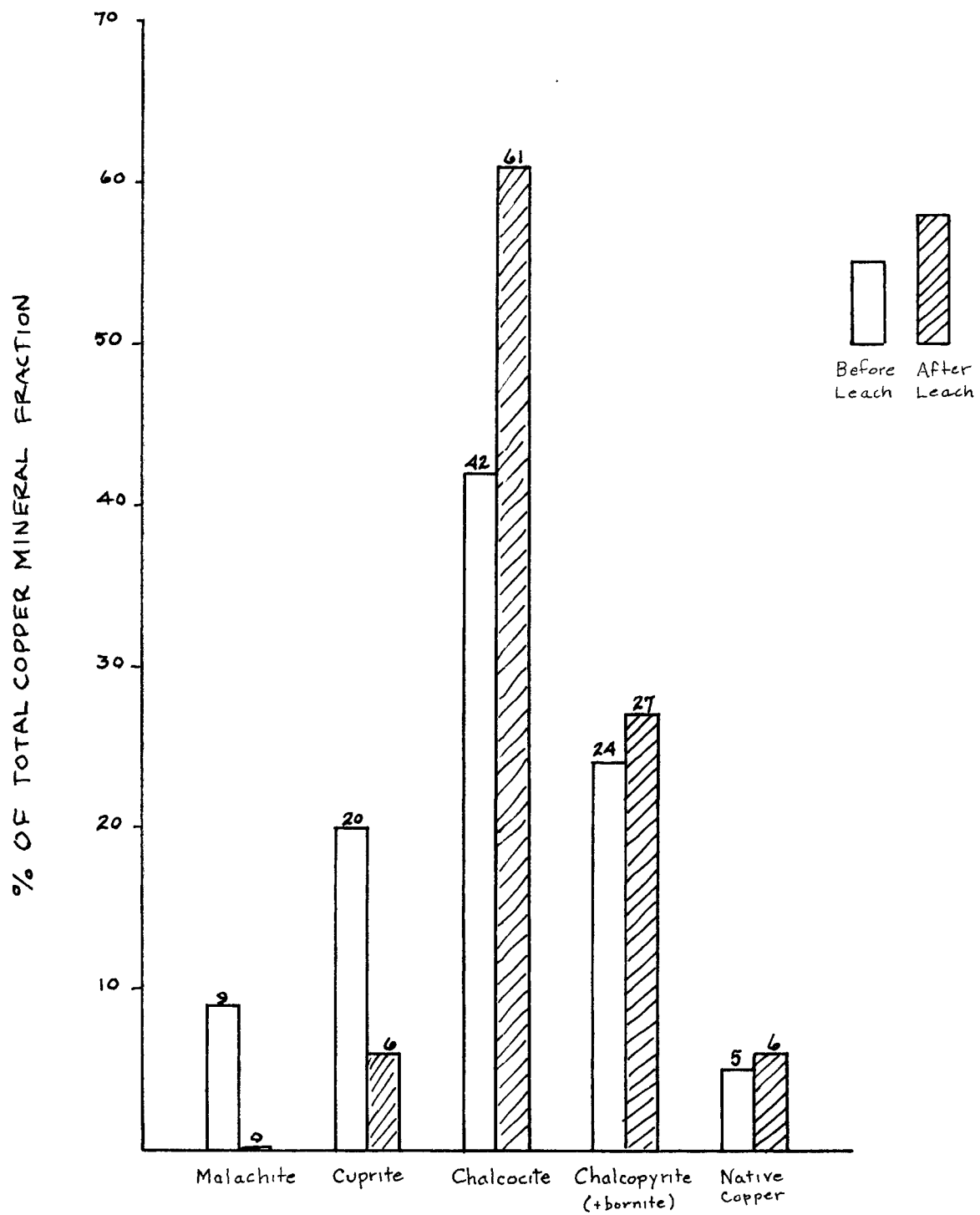


FIGURE 1: CHANGE IN RELATIVE COPPER MINERAL CONTENT OF GIBRALTAR PULPS AFTER 90-MINUTE, 30% H₂SO₄ LEACH.

1. Pure mineral specimens of chalcocite, chalcopyrite and cuprite were obtained from U.B.C. collections. Pure metallic copper was substituted for native copper. No tests were done on copper carbonates which are known to dissolve completely in H_2SO_4 .
2. Specimens were crushed and sieved to -150 mesh and +150 mesh fractions. Samples, weighing 1.0000 gm., of each fraction were weighed out.
3. Chemex Labs oxide assay procedure was duplicated by leaching one set of samples in 5% H_2SO_4 for 15, 30 and 60 minutes. After leaching, the percent soluble copper in solution was determined by atomic absorption. The insoluble mineral residue was re-weighed.
4. Placer oxide assay procedure was duplicated on a second set of samples by leaching in 30% H_2SO_4 for 60, 90 and 120 minutes. As before, the solution was run on the AA and the residue re-weighed.

TABLE 3

Controlled Mineral Leach: % Soluble Copper

Mineral	Time Min.	5% H_2SO_4		Time Min.	30% H_2SO_4	
		% Soluble Copper			% Soluble Copper	
		+150 mesh	-150 mesh		+150 mesh	-150 mesh
Chalcopyrite	15	.045	.066	60	.050	.039
	30	.060	.071	90	.046	.020
	60	.070	.136	120	.044	.034
Chalcocite	15	.068	.266	60	.070	.186
	30	.064	.264	90	.068	.170
	60	.062	.260	120	.064	.188
Cuprite	30	24.10	30.14	90	27.30	29.17
Native Copper	15	.504	no data	60	.506	no data
	30	.474	data	90	.470	data
	60	.472		120	.414	

TABLE 4

Controlled Mineral Leach: Weight % Dissolved Mineral

	Time Min.	5% H ₂ SO ₄ , -150 mesh		Time Min.	30% H ₂ SO ₄ , -150 mesh	
		Wt.insol.(gm)	Wt.% dissolved		Wt.insol.(gm)	Wt.% dissolved
Chalcopyrite	15	.9507	4.93	60	.9541	4.59
	30	.9573	4.27	90	.9498	5.02
	60	.9403	5.97	120	.9525	4.75
Chalcocite	15	.9360	6.30	60	.9431	5.69
	30	.9274	7.26	90	.9425	5.75
	60	.9269	7.31	120	.9404	5.96
Cuprite	30	.4700	53.00	90	.4564	54.36
Native Copper	15	.9934	0.66		no data	
	30	.9804	1.96			
	60	.9896	1.04			

Table 3 gives the percent soluble copper derived in each test. Table 4 gives the weight percent of copper mineral dissolved. The two sets of data are depicted in Figures 2 and 3, respectively.

Figure 2 depicts percent soluble copper, as determined by atomic absorption analysis of leach solution, plotted against leach time. Two significant and unexpected trends are evident. First, less copper is liberated from chalcopyrite, chalcocite and native copper in 30% H₂SO₄ than in 5% H₂SO₄. Second, less copper is liberated from the three minerals in a 2-hour leach than in a 15-minute leach. These results appear to conflict with standard chemical principles of greater ionic dissociation with stronger acids and longer attacks.

Figure 3 depicts the weight percent of dissolved mineral, as determined by weighing mineral residue, plotted against leach time. The same two unexpected trends are evident. Weak acid attack has dissolved about 1% more chalcocite and .5% more chalcopyrite than strong acid. Cuprite shows about 1% greater solubility in strong acid and longer leach time.

Native copper solubility data in strong acid was not obtained. However, within the two experimental groups (weak acid, 15-60 min.; strong acid, 60-120 min.) all four minerals show a general increase in solubility with time.

The above results were checked by re-runs of most tests with duplication of original results. Experimental error is not involved. A possible cause of apparent decrease in copper solubility with time and acid strength

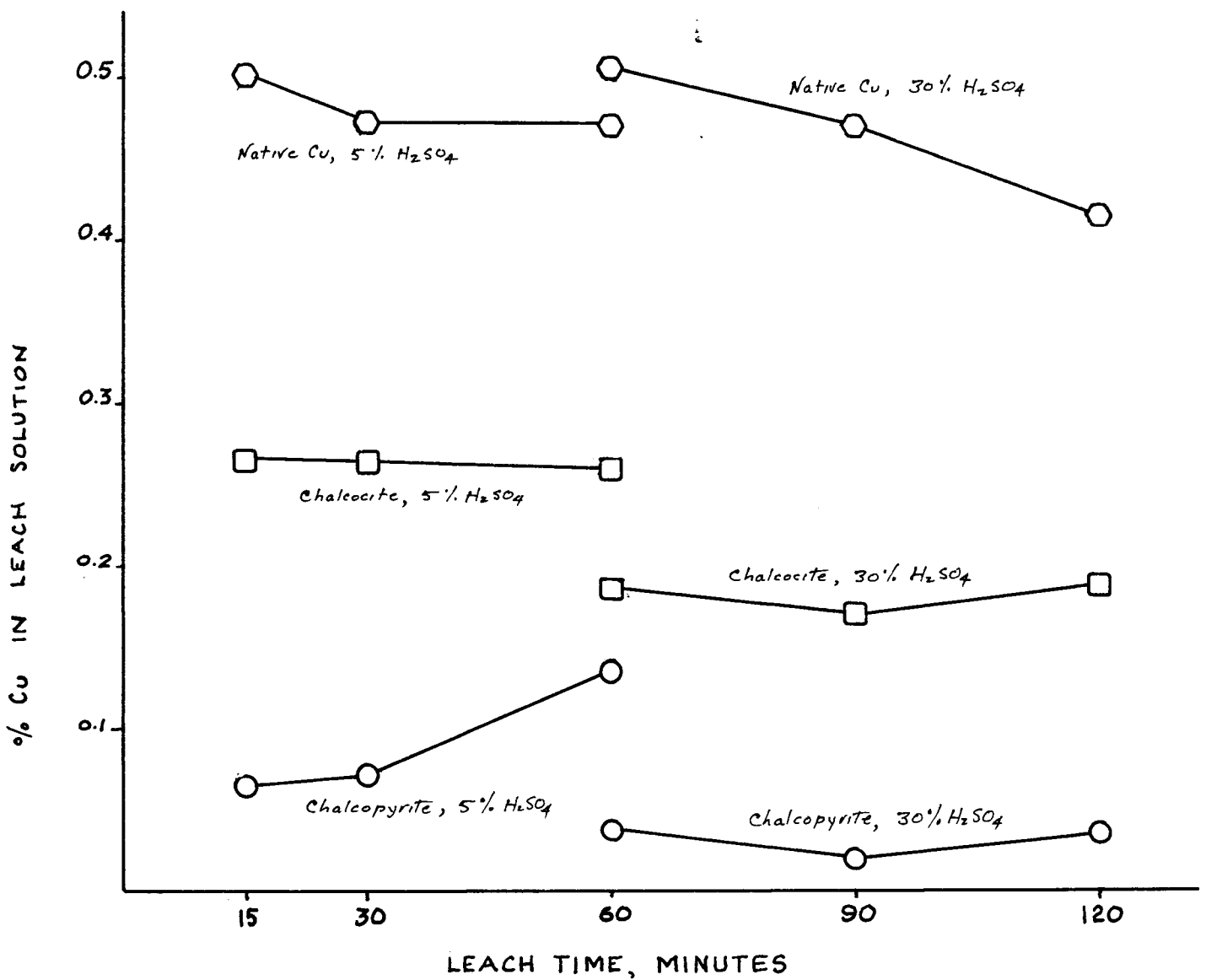


FIGURE 2 : CONTROLLED MINERAL LEACH - PERCENT SOLUBLE CU VS TIME.

Chalcopyrite and chalcocite data for -150 mesh fraction.
 Copper data for +150 mesh fraction.
 Insufficient cuprite for multiple runs.

- chalcopyrite
- chalcocite
- ◇ native Cu

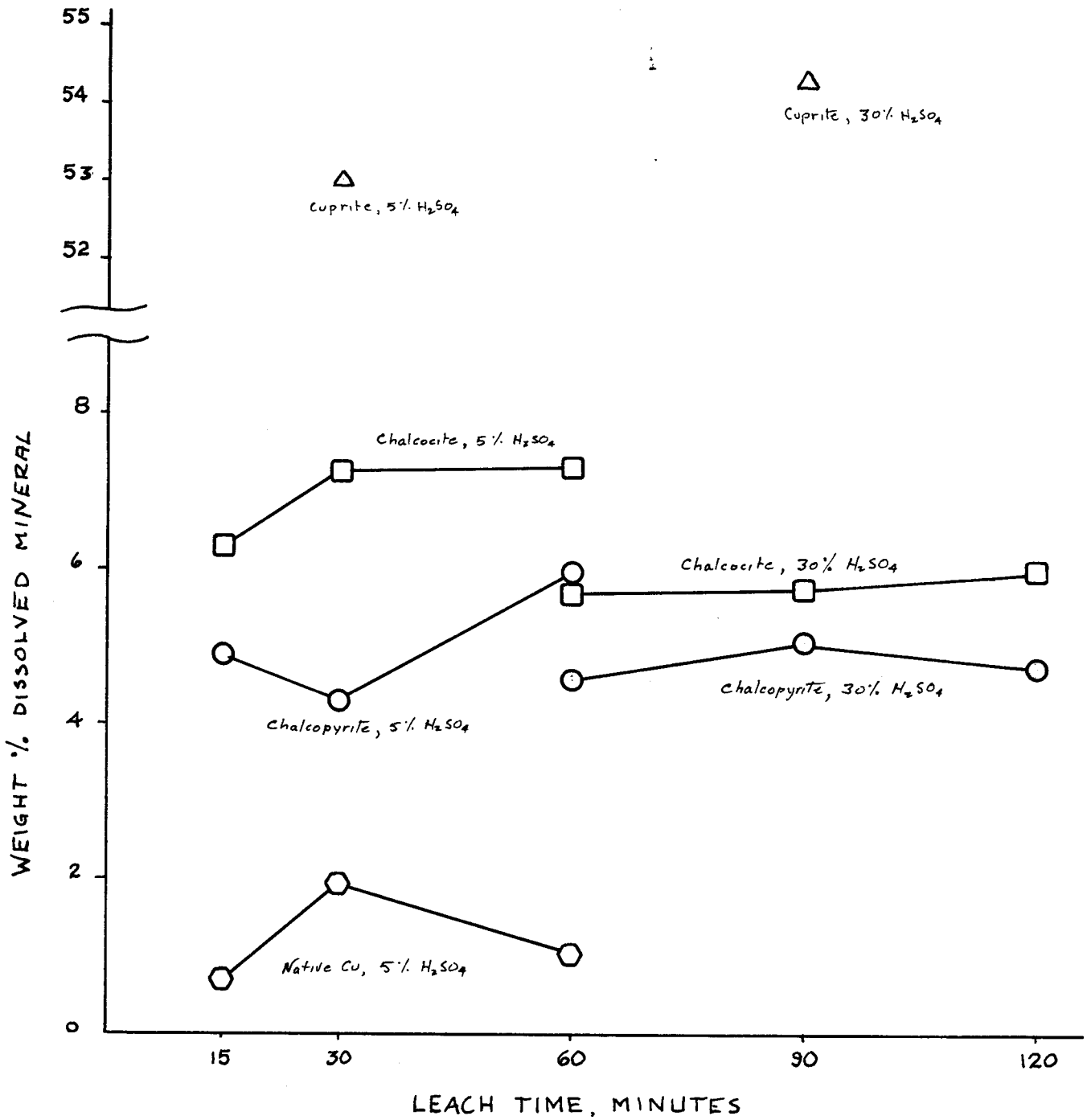


FIGURE 3: CONTROLLED MINERAL LEACH — WEIGHT PERCENT DISSOLVED MINERAL VS. TIME.

Chalcopyrite, chalcoite and cuprite data for -150 mesh fraction.
Native copper data for +150 mesh fraction.

- Chalcopyrite
- Chalcoite
- Native Cu
- △ Cuprite

may be an electrolytic re-precipitation reaction that removes copper from solution. Also, the copper ions may be oxidized by available O₂ in H₂O, and rendered unavailable to atomic absorption analysis.

The result of this reprecipitation trend should be a net reduction in the copper oxide assay by Placer technique. The percent soluble copper at 30 minutes, 5% H₂SO₄ was compared to the 90 minutes, 30% H₂SO₄ data to obtain a measure of the difference between Placer and Chemex assay techniques. The percent "correction" was applied to the weighted % contribution of each mineral to the total oxide assay (Table 5). A theoretical difference of -7% was calculated in this manner, indicating that if copper minerals in the pulps respond similarly to the experimental pure mineral specimens, Placer's oxide copper assays should be about 7% less than Chemex assays. Since the opposite trend is noted in comparative assays, it is concluded that the reprecipitation trend is dependent upon the unique experimental conditions, and is not generally applicable to leaching of pulps where the multiple elements and matrix effects apparently modify the chemical reactions.

The results of the controlled mineral leach experiment may be used to calculate the contribution of each copper mineral to the oxide assay. The average mineralogical composition of Gibraltar oxide ore is taken from Section 2. The Cu content of each mineral is taken as the theoretical maximum. The amount of mineral dissolved in oxide assaying is taken as the experimental maximum, since some reprecipitation may occur. In Table 5, the product of percent mineral content, Cu content of that mineral and amount of mineral dissolved gives, upon recalculating to 100%, the proportional contribution of each copper mineral to the copper oxide assay.

Table 5 shows that the "oxide" minerals cuprite and malachite together account for 86% of the copper oxide assay. Chalcocite contributes 11%, chalcopyrite + bornite contribute 2% and native copper about 0.5%.

TABLE 5

Proportional Contributions by Copper Minerals to Gibraltar Copper Oxide Assay

Mineral Composition	1. Cu content of mineral	2. Average % abundance	3. Amount dissolved	Product 1x2x3	Weighted % of oxide assay
Cuprite Cu ₂ O	.89	20	.65	11.57	55.3
Malachite Cu ₂ CO ₃ (OH) ₂	.72	9	1.0	6.48	31.1
Chalcocite Cu ₂ S	.80	42	.07	2.32	11.1
Chalcopyrite (+ bornite) CuFeS ₂	.34	24	.05	0.41	2.0
Native Copper Cu	1.00	5	.02	0.10	0.5
				20.88	100.0

Conclusions

1. Placer Research Center copper oxide assays are about one-third higher, on the average, than oxide assays from Chemex, Loring and Crest.
2. Chalcocite and cuprite together constitute about two-thirds of the total copper minerals in Gibraltar oxide ore. Average copper mineral content is chalcocite: 42%, chalcopyrite + bornite: 24, cuprite: 20, malachite: 9, native copper: 5.
3. Examination of pulps after leaching showed that all the carbonates dissolve plus about two-thirds of the cuprite, 5% of the chalcocite, 3 to 5% of the chalcopyrite and bornite, and about 1 to 2% of the native copper. The copper "oxide" minerals contribute the bulk of the copper oxide assay, but copper sulfides, particularly chalcocite contribute significantly.
4. Controlled leaching of copper minerals showed that more copper was liberated by weak acid attack for short periods than by strong attack up to two hours. Anomalous re-precipitation and/or oxidation effects are believed responsible for these unexpected results. The results indicate Placer oxide assays should be 7% less rather than 37% more than Chemex assays.
5. The experimental data allows calculation of the proportional contribution of each copper mineral to the Gibraltar copper oxide assay. The figures are cuprite 55%, malachite 31%, chalcocite 11%, chalcopyrite + bornite 2%, native copper .5%.
6. Copper derived from non-oxide minerals partially compensates for the undissolved portion of the cuprite fraction. The Placer oxide assay appears to be slightly low - about 5% - rather than high, as the comparison to other labs indicates. Chemex, Loring and Crest oxide assays would then be much lower than the true copper oxide content.

Respectfully submitted,



K.M. Dawson

KMD/mm
Encls.

Distribution: C.L.Pillar/E.A.Scholz/S.J.Tennant
M.Gibbs/W.Trythall/J.Knox
P.White/H.A.Steane
B.Wilson/B.Robson/J.Wilson
A.D.Drummond
J.J.Hylands

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Appendix 1

Comparison of Copper Assays on Gibraltar Drill Core

Nineteen samples were picked at random, the samples were riffled and split. One of these samples was chosen for its high oxide content and this was again split, one portion being renumbered (24978) and included with the group as a further check. This made a group of twenty samples, these were then sent to Loring Labs and also to Crest Labs for Oxide and Sulphide analysis. The results have been tabulated and are listed here. The original pulp was re-assayed by our lab, the original assay being listed as #1, the re-assay as #2 and a further assay made on the split portion sent to Loring and Crest as #3.

	PLACER						
	#1				#2		
	CuOx	CuS	Cu Total		CuOx	CuS	Cu Total
24978 *							
25760	.002	.432	.434		.004	.438	.442
25796	.003	.080	.083		.004	.078	.082
25858	.001	.090	.091		.001	.084	.085
25916	.002	.248	.250		.002	.234	.236
25976	.124	.026	.150		.123	.024	.147
25979	.022	.162	.184		.043	.158	.201
25980	.003	.224	.227		.003	.208	.211
25981	.003	.260	.263		.004	.258	.262
26041	.004	.074	.078		.011	.074	.085
25782	.003	.264	.267		.008	.268	.276
25845	.007	.106	.113		.012	.102	.114
25848	.036	.336	.372		.071	.312	.383
25978 *	.278	.047	.325		.272	.046	.318
25983	.003	.234	.237		.005	.222	.227
25993	.001	.158	.159		.001	.150	.151
25994	.001	.122	.123		.001	.116	.117
26002	.048	.244	.292		.063	.196	.259
26022	.002	.464	.468		.002	.460	.462
26042	.020	.334	.354		.025	.128	.153

* Samples 25978 and 24978 are splits of the same sample.

	PLACER #3			LORING			CREST		
	CuOx	CuS	Cu Total	CuOx	CuS	Cu Total	CuOx	CuS	Cu Total
24978 *	.265	.100	.365	.260	.110	.370	.23	.12	.35
25760	.014	.418	.432	.005	.445	.450	.01	.41	.42
25796	.010	.085	.095	.005	.085	.090	Trace	.09	.09
25858	.007	.094	.101	.005	.095	.100	Trace	.10	.10
25916	.011	.250	.261	.005	.255	.260	Trace	.25	.25
25976	.119	.028	.147	.110	.040	.150	.09	.05	.14
25979	.028	.176	.204	.020	.190	.210	.01	.19	.20
25980	.009	.224	.233	.005	.235	.240	Trace	.22	.22
25981	.015	.258	.273	.005	.265	.270	.01	.25	.26
26041	.013	.076	.089	.010	.090	.100	.01	.08	.09
25782	.023	.256	.279	.02	.27	.29	.01	.27	.28
25845	.017	.100	.117	.01	.11	.12	.01	.11	.12
25848	.082	.290	.372	.03	.35	.38	.03	.33	.36
25978 *	.272	.052	.324	.29	.05	.34	.23	.09	.32
25983	.016	.212	.228	.01	.23	.24	.01	.22	.23
25993	.007	.148	.155	.01	.15	.16	Trace	.15	.15
25994	.009	.112	.121	.01	.11	.12	Trace	.12	.12
26002	.060	.203	.263	.04	.22	.26	.04	.22	.26
26022	.015	.422	.437	.01	.44	.45	.01	.41	.42
26042	.034	.120	.154	.01	.15	.16	.02	.13	.15

$\bar{x} = .051$

$\bar{x} = .043$

$\bar{x} = .036$

The results from Crest Labs for samples 25978 down to 26042 have been re-arranged from the assay certificate issued by Crest. This is due to the fact that Crest had a mix up in their lab numbering, the error when brought to their attention was traced and the correction made.

Total copper assays on Placer run #1 for samples #26002 and #26042 would appear to be erroneous.

The average difference between this lab and Loring shows Loring higher by .004% and between Crest and this lab shows Crest lower by .006%. The agreement between all three labs is excellent, the slight differences encountered being due to the sample as indicated by the difference between the two splits of sample #25978.

B. Robson
Chief Assayer

BR/jan
April 19, 1971

cc W.S. Pentland /
B. Wilson
File