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THE SEQUENTIAL COPPER ANALYSIS METHOD—GEOLOGICAL, MINERALOGICAL, AND METALLURGICAL IMPLICATIONS

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Abstract. The sequential copper analysis method is a particularly useful technique to semi-quantitatively define the geologic, mineralogic, and metallurgical types and zonations commonly associated with porphyry-type copper deposits. The method is based on the partial dissolution behavior displayed by the prevalent copper minerals malachite, chrysocolla, chalcocite, and chalcopyrite to solutions containing sulfuric acid and sodium cyanide. Results from sequential analyses of the sample and analytical residue using sulfuric acid followed by sodium cyanide and then aqua regia solutions when compared with conventional total copper analyses can determine the amounts of leachable oxide minerals, leachable secondary sulfide minerals, and primary copper minerals, respectively. Sequential assay analytical results and interpretation are presented for copper deposits in Chile, Mexico, and the United States.

INTRODUCTION

Over the last several years, there has been a dramatic increase in the number of copper deposits using, or that are slated to use, low-cost heap leaching and solvent extraction-electrowinning processing methods. Many of these deposits are dependent on leaching ores containing a large proportion of copper oxide minerals. However, this focus on oxide only deposits is rapidly shifting toward the leaching of secondary sulfide or chalcocite-rich copper deposits. The exploration, evaluation, and ultimate development of the oxide and secondary sulfide deposits are generally predicated on the routine assaying of both surface samples and drill hole core or cuttings.

A number of different analytical procedures or methods have been utilized over the last 100 years to analyze the amount of readily leachable copper oxide mineralization within a particular assay sample. Most of these methods employ sulfuric acid as the reagent. The comparison of this oxide or acid soluble copper assay with the total copper assay has typically provided a good indication as to the distribution of copper oxide mineralization within a deposit. However, the same analytical procedures do not provide an indication as to the presence of any secondary or leachable sulfide mineralization which might be present within the deposit and which would also be leachable under similar conditions as the copper oxide mineralization.

We, herein, propose a sequential copper analysis method which, when used on geological or assay samples on a systematic basis, is able to evaluate various copper deposits, including secondary sulfide deposits, and determine their amenability to leaching as well as their mineralogical zonation and geologic type. Information of this nature is often not available or can be misleading when relying solely on visual inspection of drill samples, drill logs, or oxide copper and total copper assays. Furthermore, this method is able to semi-quantitatively define the often-noted systematic progression, in many copper deposits, from the leached cap through the copper oxide mineralized zone to the underlying secondary sulfide or enriched copper zone and the contact with the underlying primary sulfide or hypogene copper zone.

REVIEW OF PREVIOUS INVESTIGATIONS

It has long been known that most of the copper oxide minerals are readily dissolved in varying strengths of sulfuric acid solutions. Sloan (1934) has evaluated a number of different analytical methods employing sulfuric acid leaching. Several of these methods or variations of these methods are routinely used for oxide or acid soluble copper determinations at commercial laboratories in the western United States. Information regarding the dissolution behavior of a number of common copper oxide and primary sulfide copper minerals to varying strengths of sulfuric acid minerals at differing particle sizes and reaction times has been presented by Brown and Sullivan (1934).

Numerous authors have also investigated the solubility of various oxide and sulfide copper minerals to varying strengths of cyanide-containing solutions. Leaver and Woolf (1931) present information indicating that most copper oxide minerals are readily dissolved in the presence of sodium cyanide solutions as well as the important secondary sulfide copper minerals, chalcocite and covellite. However, the widespread primary copper sulfide mineral, chalcopyrite, is not readily dissolved in the presence of either sodium cyanide solutions or sulfuric acid. Investigations as to the solubility behavior of both oxide and sulfide copper minerals in the presence of sodium cyanide solutions have also been published by Hedley and Kentro (1945) and Hedley and Tabachnick (1965). The results of these previous investigations as to the solubility of various oxide, secondary sulfide, and primary sulfide copper minerals to sulfuric acid and sodium cyanide solutions are presented in Table 1, along with the idealized composition of the various mineral species. From Table 1 it can be seen that most of the copper oxide minerals are readily dissolved in both sulfuric acid and sodium cyanide solutions with the important exception that less than half of the chrysocolla is dissolved with sodium cyanide. The secondary sulfide minerals are readily dissolved in sodium cyanide solutions, but are generally unaffected by sulfuric acid. The important primary sulfide mineral, chalcopyrite, is only slightly dissolved with either sulfuric acid or sodium cyanide. With the selective application of these different dissolution characteristics to the various copper-bearing minerals, it may be possible to segregate these minerals on the basis of their dissolution characteristics--this is the basis of the sequential copper analysis method.

CURRENT ANALYTICAL INVESTIGATIONS

Because the sequential copper method is based on the differing dissolution characteristics of various copper minerals, it was necessary to independently verify and expand upon the dissolution behavior reported in Table 1. Relatively pure samples of the four common copper-bearing oxide and sulfide minerals--chrysocolla, malachite, chalcocite and chalcopyrite--were collected so that sulfuric acid and sodium cyanide dissolution tests could be performed. These four minerals commonly represent major mineral species present in many copper deposits and should provide an adequate indication of the behavior of oxide, secondary sulfide minerals, and primary copper mineralization to different dissolution methods. Malachite was obtained from the old Castle Dome Mine and chrysocolla from the old Inspiration pit, both in the Globe-Miami District of Arizona; chalcocite was obtained from the Ray Mine in Arizona; and chalcopyrite was obtained from the United Verde pit at Jerome, Arizona. These individual samples were closely inspected and trimmed to make sure that no other copper-bearing minerals were included and then crushed and ground, and a minus 150-mesh pulp prepared.

The pulps were then analyzed for total copper as well as copper dissolved using three typical sulfuric acid soluble dissolution methods and one sodium cyanide method. Based on the comparison of the total copper values determined with the theoretical copper amounts in pure samples, it appears that the malachite sample is approximately 97 percent pure; chrysocolla is approximately 70 percent pure; chalcocite 88 percent pure; and chalcopyrite 80 percent pure. The four mineral samples were analyzed at two separate commercial labs in Tucson, Arizona, both of which gave very similar results for the tests performed. The relatively pure samples were then diluted with pure silica sand to produce new samples assaying near one percent total copper. The diluted samples were reground to minus 150-mesh; assay pulps prepared and subjected to the same total copper and partial copper extraction tests as for the pure samples; and all four samples returned comparable percentage dissolution results. Furthermore, results from both labs were again very similar. The results of these investigations on pure and diluted samples are presented in Table 2. A brief description of the five analytical methods used to generate the results shown in Table 2 is presented in Table 3. Comparison of the results obtained from the three different sulfuric acid dissolution methods employed at the two different labs suggests that while they all give quite similar results, the shake leach acid soluble copper method employed at Lab 1 generally gives a slightly higher percentage dissolution of both the pure and diluted prepared samples. Because of the importance of complete dissolution, particularly for the copper oxide minerals, this analytical method was utilized for all further sulfuric acid dissolution test work.

The percentage dissolution results from all methods as reported in Table 2 are generally comparable to, or in the same range as, those presented in Table 1 from the previous investigations reported in the literature. In summary, the dissolution behavior of both the pure and diluted samples of the four copper minerals evaluated behaved similarly to that predicted, based on the results from previous investigations. By analogy, it is expected that the dissolution characteristics for the other minerals listed on Table 1, but not independently evaluated here, are also broadly confirmed.

Because most copper deposits rarely exhibit mineralized zones comprised of a single copper mineral, tests were conducted blending the four copper minerals utilized earlier--chrysocolla, malachite, chalcocite, and chalcopyrite--together in varying percentages which would relate to the possible zonation within a copper deposit from an oxide-only zone to an underlying zone containing significant amounts of secondary sulfide copper minerals and into an underlying transitional zone containing an appreciable amount of chalcopyrite. The analytical results for the blended-prepared samples are presented in Table 4. It was found that the blended samples dissolved in a regular and predictable fashion in amounts similar to that obtained from the individual samples, hence, there does not appear to be any significant interference effects using the acid soluble and cyanide soluble methods.

THE SEQUENTIAL COPPER ANALYSIS METHOD

Investigations conducted on various ores containing the copper minerals included in Table 1, in both metallurgical test columns and under pad and heap-leaching conditions, have demonstrated their dissolution behavior and provide the metallurgical basis for development and application of the sequential copper analysis method. Under these conditions, it has been found that sulfuric acid leaching is generally quite successful in recovering a large percentage of copper from copper oxide minerals, closely approaching the values for the specific minerals as shown in Tables 1 or 2 over relatively short leaching times--less than 100 days. In contrast, leaching with sulfuric acid under both laboratory and commercial-scale conditions dissolves only very small amounts of secondary and primary sulfide minerals. Similar lab and commercial-scale testing utilizing oxidizing agents, such as ferric iron, in combination with sulfuric acid have demonstrated that both oxide and secondary sulfide minerals are quite thoroughly leached over longer periods--exceeding 100 days. With the exception of chrysocola, leaching behavior of copper-bearing minerals under ferric-iron/sulfuric acid leaching is generally closely modelled by dissolution with sodium cyanide of assay-type samples. Primary sulfide minerals, such as chalcopyrite, are essentially unleachable under laboratory or commercial-scale conditions using any of the previously mentioned conditions or reagents, even over very long periods.

Because of the different dissolution characteristics of the oxide, secondary sulfide, and primary sulfide minerals to the different partial extraction copper laboratory analytical methods (sulfuric acid and sodium cyanide soluble copper), it is possible, by first subjecting the assay sample to sulfuric acid digestion followed by the sodium cyanide dissolution and then analyzing the sample residue for total copper in a sequential fashion, that one can selectively leach or analyze for the different mineral types present in a particular sample and effectively model the sample's metallurgical behavior. The shake leach sulfuric acid soluble assay method attacks and quite thoroughly dissolves nearly all of the significant copper oxide minerals present, which are also amenable to standard sulfuric acid leaching conditions. If the same samples are then subjected to a sodium cyanide soluble assay, the secondary sulfide minerals and bornite would be dissolved and would represent that proportion of the sample which would be amenable to ferric-iron/sulfuric acid leaching methods. A total copper assay of the analytical residue following the sulfuric acid and cyanide dissolution steps will determine the amount of copper not dissolved by these two laboratory extraction methods and, by analogy, the proportion of copper in the sample not amenable to relatively rapid leaching. This residue will contain insoluble primary copper sulfide minerals, primarily chalcopyrite, which requires bacteriological activity and a much longer time frame to recover through leaching.

To test the sequential assay method and its ability to semi-quantitatively determine the mineralogical types present in a given sample, the same set of blended-prepared samples utilized in Table 4 were analyzed using the sequential assay method with the results presented in Table 5. With a total copper analysis of approximately one percent for each of the five samples, the results for each analytical step behaved fairly close to what was predicted based on the results shown in Table 1. The slight solubility of chalcocite in sulfuric acid is demonstrated, as is the near total insolubility of chalcopyrite, which is reflected in the residue total copper analysis. Furthermore, the summed total of the acid soluble, cyanide soluble, and residual assays closely matched the beginning total copper analysis, providing a check on the reproducibility and accuracy of the sequential assay steps.

The procedures used in the sequential copper method as developed and utilized by a major commercial laboratory in Arizona are presented in Table 6.

DISCUSSION

A proposed geological, mineralogical, and metallurgical classification scheme based on the results obtained from the sequential copper analysis method is presented in Table 7. This table provides a summary of the information presented earlier and suggests a method for the semi-quantitative definition of geological zones often recognized in various copper deposits. This geological classification is based on the ratios of the soluble and residual copper assays to that of the total copper assay, utilizing results from the four-step sequential copper analysis method.

To further test the validity and applicability of the sequential assay method, assay pulps from selected drill holes from the Suaqui Verde copper deposit in Sonora, Mexico, and the Andacollo copper deposit, Region IV, Chile, were tested, with the results presented as Tables 8 and 9, respectively. Also presented in these tables is the proposed geological classification of these samples based on the sequential copper assays. Both of these deposits were difficult to evaluate for their leachable copper resources because they contain a significant portion of their mineralization within leachable secondary sulfide copper minerals, primarily chalcocite. Using only conventional total copper and oxide or acid soluble copper analyses from the drill samples, it was not possible, in many cases, to accurately portray or classify the different mineralogical or geological zones present in these deposits because leachable sulfide minerals were not distinguished from non-leachable primary sulfide minerals. In both of these deposits, it was also difficult to consistently and accurately define the mineral zones by visual examination or logging of drill core or cuttings. For the drill samples analyzed in Tables 8 and 9, there appears to be relatively good definition of the different geological zones, as well as good correlation between the total and summed total copper contents. Duplicate analyses have indicated that total copper analyses are generally reproducible to close tolerances, generally ±5 percent. However, duplicate sulfuric acid and sodium cyanide soluble analyses suggest they are reproducible to a lesser degree, typically ±15 percent, and hence, the results from the sequential copper method should be considered semi-quantitative.

The sequential assay method can also be used to assist in the definition of a metallurgical test program, as well as evaluating test results. Being able to define the various metallurgical and mineralogical types present, as well as their relative overall proportions within the deposit, allows for the selection of more accurate representative samples for metallurgical testing. Sequential copper analyses performed on pre-leaching head and post-leaching tail samples from metallurgical test work can provide valuable information relating to the percent extraction or leaching efficiency of each of the mineralogical types present in the sample and aid in selection of the most appropriate leaching parameters.

As an example, Table 10 presents analytical information on head and tail samples from two metallurgical columns from the Carlota copper deposit in Arizona. The assay results indicate that chalcocite is the predominant copper-bearing mineral in the two samples and was quite thoroughly leached during the duration of the tests, which were conducted using a ferric iron/sulfuric acid reagent.

CONCLUSIONS

The sequential copper analysis method appears to be a particularly useful technique to quite accurately determine the different geological and mineralogical zonations commonly found within a typical copper deposit and should be considered whenever conventional total and sulfuric acid soluble copper analyses indicate a significant proportion of sulfide mineralization. The sum of the copper dissolved during the sulfuric acid and sodium cyanide soluble assay steps has been shown to semi-quantitatively determine the amount of copper which may be leachable under established heap or pad leaching conditions. The sequential assay method is also helpful in designing an appropriate metallurgical testing program, selecting representative samples, and evaluating the potential effectiveness of the metallurgical procedure in the recovery of the minerals of interest. The routine application of this method to develop semi-quantitative assay information from each drill hole will also aid in the definition of different geologic and mineralogic zones and their related leachable copper components which can then be integrated into the ore reserve modelling process.

The importance of petrographic work to establish the variety of different mineral species and their general distribution should not be overlooked and indeed should form the underlying basis upon which to routinely apply the sequential copper assay method. In addition, petrographic work on the residual products from the sequential assaying of metallurgical or other samples is also warranted as a check of the effectiveness of the preceding dissolution steps.

The sequential copper analysis method presents no significant technical problems and likely can be easily implemented by most commercial assay laboratories. On a production basis at a commercial-scale lab, estimated costs for each step of the four-step sequential assay method have been estimated at approximately US$4 to $5 or approximately US$20 for each sample, excluding sample preparation or pulping costs. If total copper analyses have already been performed, then only three sequential steps need to be performed at a comparatively lower cost. Where appropriate, significant cost savings may also be realized if the sequential assay method is utilized on assay pulps which may be composited over multiple sample intervals.

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TABLE 1

Approximate Percentage Dissolution of Various Copper Minerals to Sulfuric Acid and Sodium Cyanide Solutions

Mineral Species	Approximate Composition	Approximate Dissolution in Sulfuric Acid Solution	Approximate Dissolution Sodium Cyanide Solution
OXIDES			
Atacamite	$Cu_2CL(OH)_3$	100	100
Azurite	$2CuCO_3Cu(OH)_2$	100	100
Cuprite	Cu_2O	70	100
Chrysocolla	$CuSiO_32(H_2O)$	100	45
Malachite	$CuCO_3Cu(OH)_2$	100	100
Native Copper	Cu	5	100
Tenorite	CuO	100	100
SECONDARY SULFIDES			
Chalcocite	Cu_2S	3	100
Covellite	CuS	5	100
PRIMARY SULFIDES			
Bornite	Cu_5FeS_4	2	100
Chalcopyrite	$CuFeS_2$	2	7

NOTE: Samples are generally finely ground (-150 mesh) and reaction time is generally one hour or less.

TABLE 2

Analytical Results for Pure and Diluted Samples
Analytical Method

Sample	Lab	Total Copper Digestion % Cu	% Diss	Lab 1 Standard Acid Soluble % Cu	% Diss	Lab 1 Shake Leach Acid Soluble % Cu	% Diss	Lab 2 Standard Acid Soluble % Cu	% Diss	Sodium Cyanide Soluble Copper % Cu	% Diss
Pure Chrysocolla	Lab 1	22.1	100	21.40	96.8	21.9	99.1	21.8	98.6	12.10	54.8
	Lab 2	21.2	100					20.2	95.3	9.92	46.8
Pure Malachite	Lab 1	55.8	100	54.70	98.0	55.4	99.3	55.0	98.6	54.5	97.7
	Lab 2	55.9	100					52.6	94.1	48.0	85.9
Pure Chalcocite	Lab 1	70.4	100	2.03	2.9	2.90	4.1	2.80	4.0	68.8	97.7
	Lab 2	70.5	100					0.64	0.9	66.9	94.9
Pure Chalcopyrite	Lab 1	27.7	100	0.73	2.6	0.33	1.2	0.32	1.2	1.66	6.0
	Lab 2	27.5	100					0.26	0.9	1.34	4.9
Diluted Chrysocolla	Lab 1	1.00	100	0.69	69.0	0.99	99.0	1.00	100	0.52	52.0
	Lab 2	0.99	100					0.97	98.0	0.32	32.3
Diluted Malachite	Lab 1	0.97	100	0.72	74.2	0.99	102	0.97	100	0.97	100
	Lab 2	0.90	100					0.88	97.8	0.90	100
Diluted Chalcocite	Lab 1	1.04	100	0.019	1.8	0.087	8.4	0.070	6.7	0.99	95.2
	Lab 2	0.98	100					0.090	9.2	0.98	100
Diluted Chalcopyrite	Lab 1	1.02	100	0.023	2.3	0.030	2.9	0.023	2.3	0.082	8.0
	Lab 2	0.94	100					0.034	3.6	0.061	6.5

TABLE 3

Description of Analytical Methods

Method	Description
Total Copper - same at both labs	0.200 gram sample, digestion with hydrochloric (HCL), nitric (HNO_3) and perchloric ($HCLO_4$) acid, read on AA.
Lab 1 - Standard Acid Soluble Copper	0.500 gram sample, digestion with 100 ml. of 5% sulfuric (H_2SO_4) acid and 10 ml. of 6% sulfurous (H_2SO_3) acid, bring rapidly to a boil and boil for 5 minutes, read on AA.
Lab 1 - Shake Leach Acid Soluble Copper	0.500 gram sample, digestion with 25 ml. of 4% sulfuric (H_2SO_4) acid on shaking table at room temperature (25°C) for one hour (60 minutes), read on AA.
Lab 2 - Standard Acid Soluble Copper	0.500 gram sample, digestion with 15 ml. of 5% sulfuric (H_2SO_4) acid on shaking table at room temperature (25°C) for one hour, read on AA.
Sodium Cyanide Soluble Copper - same at both labs	0.500 gram sample, digestion with 25 ml. of 10% sodium cyanide (NaCn) on shaking table at room temperature (25°C) for one-half hour (30 minutes), read on AA.

TABLE 4

Analytical Results for Prepared Blended Samples

Sample	Total Copper % Cu	Sulfuric Acid Soluble Copper % Cu	% Diss	Sodium Cyanide Soluble Copper % Cu	% Diss
50% Cu from Chrysocolla 50% Cu from Malachite	1.00	1.00	100	0.75	75.0
50% Cu from Malachite 50% Cu from Chalcocite	1.00	0.55	55.0	0.99	99.0
50% Cu from Chrysocolla 50% Cu from Chalcocite	1.01	0.54	53.5	0.75	74.3
25% Cu from Chrysocolla 25% Cu from Malachite 50% Cu from Chalcocite	0.98	0.54	55.1	0.88	89.8
25% Cu from Chrysocolla 25% Cu from Malachite 25% Cu from Chalcocite 25% Cu from Chalcopyrite	0.98	0.53	54.1	0.65	66.3

TABLE 5

Sequential Copper Analyses for Blended-Prepared Samples

Sample	Assay Total Copper % Cu	Sulfuric Acid Soluble Copper % Cu	Sodium Cyanide Soluble Copper % Cu	Residue Total Copper % Cu	Summed Total Copper % Cu
0.50% Cu from Chrysocolla 0.50% Cu from Malachite	1.00	1.00	0.004	<0.002	1.00
0.50% Cu from Chalcocite 0.50% Cu from Malachite	1.00	0.59	0.40	<0.002	0.99
0.50% Cu from Chrysocolla 0.50% Cu from Chalcocite	1.00	0.59	0.40	0.002	0.99
0.25% Cu from Chrysocolla 0.25% Cu from Malachite 0.50% Cu from Chalcocite	1.00	0.61	0.38	0.002	0.99
0.25% Cu from Chrysocolla 0.25% Cu from Malachite 0.25% Cu from Chalcocite 0.25% Cu from Chalcopyrite	1.00	0.56	0.22	0.19	0.97

* NOTE: Acid Soluble + Cyanide Soluble + Residue Equals Summed Total Copper

TABLE 6

Analytical Procedures Used in the Sequential Copper Analysis Method

Step	Description
Total Copper	.500 gram sample, digestion with 10 ml concentrated hydrochloric (HCL), 3 ml concentrated nitric (HNO_3), and 1.5 ml concentrated perchloric ($HCLO_4$) acids to heavy $HCLO_4$ fumes, then boiled up in 10 ml concentrated hydrochloric (HCL) acid and diluted with water to 200 ml and a 5% acid solution. Digestion takes 1½ to 2 hours. Read on AA.
Sulfuric Acid Soluble Copper	0.500 gram sample, digestion in long tubes with 20 ml of 5% sulfuric (H_2SO_4) acid on mechanical shaker table at room temperature (25° C) for one hour (60 minutes). Then centrifuge sample and decant solution to 200 ml flask. Residue is washed two times with 40 ml water by shaking, centrifuging, and decanting with wash solutions added to 200 ml flask. Read leach solution in 200 ml flask on AA.
Sodium Cyanide Soluble Copper	Residue from acid soluble step is digested with 20 ml of 10% sodium cyanide (NaCN) solution on mechanical shaker table at room temperature (25° C) for one-half hour (30 minutes). Centrifuge and wash sample as per acid soluble step. Read leach solution on AA.
Residue Total Copper	Residue from cyanide soluble step is transferred into 200 ml flask and digested as per total copper step above.

TABLE 7

Proposed Mineralogical, Metallurgical, and Geological Classifications Based on Sequential Copper Analyses

Sequential Assay Step	Mineralogic Classification	Metallurgical Classification	Geological Classification	
Sulfuric Acid Soluble	Copper Oxides	Sulfuric Acid Leachable	Oxide Zone - Acid Sol/Total > 50%	Mixed Zone Acid, Cyanide, or Residue/ Total are all < 50%
Sodium Cyanide Soluble	Secondary Sulfides Component	Ferric Leachable Component	Secondary Zone - Cyanide Sol/Total > 50%	
Residue Total	Primary Sulfides	Bacterial Leachable Component	Primary Zone Residue/Total > 50%	

TABLE 8

Sequential Copper Analysis of Drill Hole Samples from the Suaqui Verde Deposit, Sonora, Mexico

Drill Hole Number and Depth Interval	Total Assay Copper % Cu	Sulfuric Acid Soluble Copper % Cu	Sodium Cyanide Soluble Copper % Cu	Residue Total Copper % Cu	Summed Total Copper % Cu	Geologic Class
SVR-3-91 120-125	0.28	0.248	0.004	0.028	0.280	Oxide
SVR-3-91 125-130	0.22	0.174	0.002	0.036	0.212	Oxide
SVR-3-91 130-135	0.59	0.248	0.143	0.174	0.565	Mixed
SVR-3-91 135-140	0.82	0.329	0.347	0.147	0.823	Secondary
SVR-3-91 140-145	0.32	0.067	0.058	0.180	0.305	Primary
SVR-3-91 145-150	0.25	0.072	0.024	0.140	0.236	Primary
SVR-8-91 20-25	0.25	0.201	0.008	0.051	0.260	Oxide
SVR-8-91 25-30	0.09	0.036	0.010	0.036	0.082	Mixed
SVR-8-91 30-35	0.34	0.090	0.164	0.188	0.342	Primary
SVR-8-91 35-40	0.78	0.238	0.337	0.213	0.788	Mixed
SVR-8-91 40-45	0.39	0.096	0.105	0.199	0.400	Mixed
SVR-8-91 45-50	0.34	0.038	0.018	0.282	0.338	Primary
SVR-14-91 20-25	0.58	0.522	0.036	0.049	0.607	Oxide
SVR-14-91 25-30	0.63	0.570	0.024	0.044	0.638	Oxide
SVR-14-91 30-35	0.24	0.098	0.058	0.070	0.226	Mixed
SVR-14-91 35-40	0.42	0.204	0.053	0.145	0.402	Mixed
SVR-14-91 40-45	0.37	0.092	0.028	0.236	0.356	Primary
SVR-14-91 45-50	0.38	0.015	0.010	0.323	0.348	Primary

*NOTE: Acid Soluble + Cyanide Soluble + Residue Equals Summed Total Copper

TABLE 9

Sequential Copper Analysis of Drill Hole Samples from the Andacollo Deposit, Region IV, Chile

Drill Hole Number and Depth Interval	Total Assay Copper % Cu	Sulfuric Acid Soluble Copper % Cu	Sodium Cyanide Soluble Copper % Cu	Residue Total Copper % Cu	Summed Total Copper % Cu	Geologic Class
91-04 57-74	0.90	0.26	0.69	0.058	1.008	Secondary
91-29 34-64	1.62	1.19	0.51	0.153	1.853	Oxide
91-29 64-80	1.15	0.32	0.70	0.090	1.110	Secondary
91-29 80-104	2.36	1.18	1.07	0.163	2.413	Oxide
91-30 24-36	0.81	0.21	0.57	0.015	0.795	Secondary
91-30 36-48	0.47	0.11	0.28	0.049	0.439	Secondary

* NOTE: Acid Soluble + Cyanide Soluble + Residue Equals Summed Total Copper

TABLE 10

Sequential Copper Analysis of Metallurgical Column Samples from the Carlota Project, Arizona

Sample Description	Total Assay Copper % Cu	Sulfuric Acid Soluble Copper % Cu	Sodium Cyanide Soluble Copper % Cu	Residue Total Copper % Cu	Summed Total Copper % Cu	Geologic Class
CS92-09 Head	0.664	0.141	0.520	0.003	0.664	Secondary
CS92-09 Tail	0.109	0.012	0.088	0.003	0.103	Secondary
% Etract 1.00-Tail/Head Assay	83.6	91.5	83.1	0.00	84.5	
CS92-10 Head	0.467	0.090	0.370	0.003	0.463	Secondary
CS92-10 Tail	0.074	0.008	0.058	0.003	0.067	Secondary
% Extract 1.00-Tail/Head Assay	84.2	91.1	84.3	0.00	85.6	

* NOTE: Acid Soluble + Cyanide Soluble + Residue Equals Summed Total Copper