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The assessment of the monitoring data from the Cyprus Sierrita Mine also provided another example in which the trace metal components migrated more slowly than the geochemical fingerprint. Although tailings leachate was present at Wells MH-14 and MH-15 for more than three years, as indicated by the geochemical fingerprint, the higher trace metal concentrations associated with the leachate were not in evidence. The significance of this observation is that trace metals would not be suitable monitoring parameters for early detection of tailings leachate migration.

6.4 Zonia Copper Mine

The final Arizona copper mining facility to be summarized is the Zonia Mine. The data set that was reviewed was incomplete because it did not contain any monitoring results for the tailings basin and the data were further limited by some readily identifiable data quality concerns. However, the ground-water monitoring data from this site still illustrate the potential of using geochemical monitoring results to fingerprint mine leachates.

A site map for the Zonia Mine is shown in Figure 6-36. The site monitoring program includes at least one well upgradient of the leaching basins (Well A-16), a series of wells that are east and downgradient of the leaching basins (Well Z-601, cabin well, Well Z-602, and Well Z-605), and several additional on-site wells. Each location was sampled on 10 occasions between 1993 and 1994 and the collected samples were analyzed for most of the common geochemical parameters, pH, total dissolved solids, and 11 trace metals for which drinking water criteria have been established.

6.4.1 Background Ground-Water Conditions

The geochemical monitoring results from upgradient Well A-16 are summarized in Figure 6-37. These data define a pattern in which alkalinity is the most abundant constituent and calcium and sulfate are the second most abundant constituents. This fingerprint, which is similar to that observed upgradient of other copper mines, had a reproducibility of 76 percent.

6.4.2 Downgradient Ground-Water Conditions

The geochemical monitoring results from Well Z601, a location approximately 1500 feet northeast of the ore processing facility, are presented in Figure 6-38. The geochemical fingerprint at this location is defined by 50 percent alkalinity, 20 percent sulfate, and small quantities of the other geochemical parameters. This pattern had a reproducibility of 94 percent. The similarity of this pattern with that at upgradient Well A-16, a 74 percent match, suggests that mine waste leachate has not impacted this location.

Data from the Old Mill well at this site have been summarized in Figure 6-39. There is an obvious data quality problem with the December, 1994 survey because the ionic sum equals more than 140 percent of the total dissolved solids concentration. However, except for the variability associated with the small calcium peak, these results define a repetitious pattern in which sulfate is the single dominant peak. The reproducibility of this pattern was estimated by regression analysis to be 86 percent.

The geochemical fingerprint at the Old Mill well represents a distinctive shift from the observed pattern at Well A-16. The sulfate-rich, alkalinity-poor pattern at the Old Mill well is only a 12 percent match for the alkalinity-rich, sulfate-poor pattern at the upgradient well. Although the data file for this mine did not contain any information on the raffinate pond or the tailings ponds, these results suggest that the ground water has been impacted by mine waste leachate because the geochemical fingerprint at the Old Mill well is similar to tailings leachate fingerprints at other copper mines (Figure 6-2, Figure 6-22, and Figure 6-32) and the fact that this pattern represents a characteristic shift from background conditions upgradient of the site.

Well A-14 is an on-site well located approximately 500 feet east of the raffinate ponds. Normalized geochemical monitoring results from this well define a consistent pattern in which sulfate is the most abundant ion, calcium is the second most abundant ion, and alkalinity is the third most abundant ion (Figure 6-40). This pattern had a reproducibility of 85 percent based on the results of 11 surveys conducted between March, 1993 and December, 1994. The sulfate-rich geochemical fingerprint at Well A-14 is very similar to the geochemical fingerprint at the Old Mill well but only has a 22 percent match with the upgradient fingerprint at Well A-16. These results also suggest that ground water at the site has been impacted by mine waste leachate.

Well Z605 is located approximately 1000 feet from an existing leach basin and close to the southern boundary of the Zonia Mine (Figure 6-36. The geochemical results from this well define a consistent, repetitive pattern in which sulfate represents approximately 60 percent of the total dissolved solids concentration (Figure 6-41). The reproducibility of the geochemical fingerprint was estimated by regression analysis to be 93 percent.

The geochemical fingerprint at Well Z605 is identical to that observed at the Old Mill well (Figure 6-39) and Well A-14 (Figure 6-40) but different from the alkalinity-rich, sulfate-poor pattern observed at upgradient Well A-16 and Well Z601. On the assumption that this pattern is indicative of copper mine waste leachate (Figure 6-2, Figure 6-22, and Figure 6-32), these results indicate that fugitive emissions from the Zonia Mine have impacted the ground water. More importantly, this set of data provides another indication that a mine waste leachate fingerprint can and will maintain its chemical identity as it migrates away from the source.

The results from one final ground-water monitoring location at the Zonia Mine are summarized in Figure 6-42. This particular set of data is presented because it illustrates the data quality problems that were present and the ability of this approach to detect them. An inspection of the results from Well Z603 indicates that sulfate represented more than 150 percent of the total dissolved solids concentration in two surveys, that total trace metals represented 50 percent of the total dissolved solids concentration in the same surveys, and calcium and sulfate each represented 100 percent of the total dissolved solids concentration in another survey. Since these conditions are not possible because the sum of the ions must equal the total dissolved solids concentration, the individual analyses are biased high and/or the total dissolved solids concentrations are biased low. If this assessment technique were applied as the data were being produced, it would be a relatively simple matter to identify the source of the error and institute corrective action in order to produce data of acceptable quality. When the flagged data are omitted, the remaining results at Well Z603 define a sulfate-rich, alkalinity-poor pattern that is similar to that at the Old Mill well and has a reproducibility of 94 percent.

6.4.3 Zonia Summary

Despite the limitations due to data quality, the monitoring results from 11 locations at the Zonia Mine only describe two geochemical fingerprints. The ground water at upgradient Well A-16 has a low total dissolved solids concentration and a fingerprint pattern that is characterized by a high relative abundance of alkalinity and a low relative abundance of sulfate. The ground water at four other wells also has a low total dissolved solids concentration and an alkalinity-rich, sulfate-poor fingerprint that is a fair to good match for the upgradient conditions (Table 6-8). However, ground water from three locations near the mine operation (Old Mill well, Instrument Shack well, and Well A-14) have elevated levels of total dissolved solids and a sulfate-rich, alkalinity-poor fingerprint that is not similar to upgradient conditions (Table 6-8). Although monitoring results for the Zonia raffinate pond or tailings ponds were not recovered during the records search, this geochemical fingerprint is identical to the characteristic tailings leachate fingerprint observed at three other Arizona copper mines. These results suggest that fugitive mine waste leachate is responsible for the altered ground-water composition at these locations.

Ground water at three locations downgradient of the mine (Well Z602, Well Z603, and Well Z605) has total dissolved solids concentrations above background levels and a consistent alkalinity-poor, sulfate-rich composition (Table 6-8). Since these conditions are a poor match for the ground water upgradient of the mine (8 to 24 percent match) but very similar to ground water conditions at the mine site (Old Mill well, Instrument Shack well, and Well A-14), the geochemical fingerprint analysis suggests that these areas have also been impacted by mine waste leachate. In addition, because these monitoring wells are located approximately 1000 feet from the ore processing facilities, these results provide further evidence that mine waste leachates maintain their characteristic geochemical identity as they migrate away from the source.

This case study also demonstrated the ability to identify suspect quality monitoring data with the geochemical fingerprint analysis technique. The highly variable concentrations in mine tailings leachates can complicate any attempt to assess data quality using conventional techniques. However, since the sum of the individual geochemical ions must be less than or equal to the total dissolved solids concentration, the ratio of concentration to total dissolved solids must be less than 1.0 for each geochemical parameter and the sum of the normalized values must be within prescribed limits (the data quality objective used during this project was that the sum of the ions should represent at least 80 percent but no more than 120 percent of the total dissolved solids concentration). An inspection of the graphical fingerprints readily identifies data sets that fail to meet these objectives without the need for extensive replicate analysis of samples or complicated statistical analysis of the results.

6.5 Discussion of Copper Mine Case Studies

The initial objective of this project was to identify appropriate monitoring parameters for cyanide heap leaching facilities. As the initial results began to indicate that geochemical parameters could be used to fingerprint the process solutions and tailings leachates at gold mines, the scope of the project was expanded to include copper mines. The data used in this study were provided by the Arizona Department of Environmental Quality.

The monitoring results from the individual mines were compiled to characterize the composition of tailings leachates at copper mines (Chapter 3). This information indicated that copper tailings leachates shared many of the same properties as process solutions and tailings leachates at heap leaching facilities. Specifically, (1) the concentrations for each constituent were highly variable and most were non-normally distributed, (2) the total dissolved solids concentration for tailings leachates were very high and averaged 10,000 mg/L, (3) a small number of common geochemical ions were repeatedly present as the most abundant constituents in the leachates, and (4) at least 15 constituents are present at concentrations that could potentially degrade water environmental conditions in the vicinity of a mine.

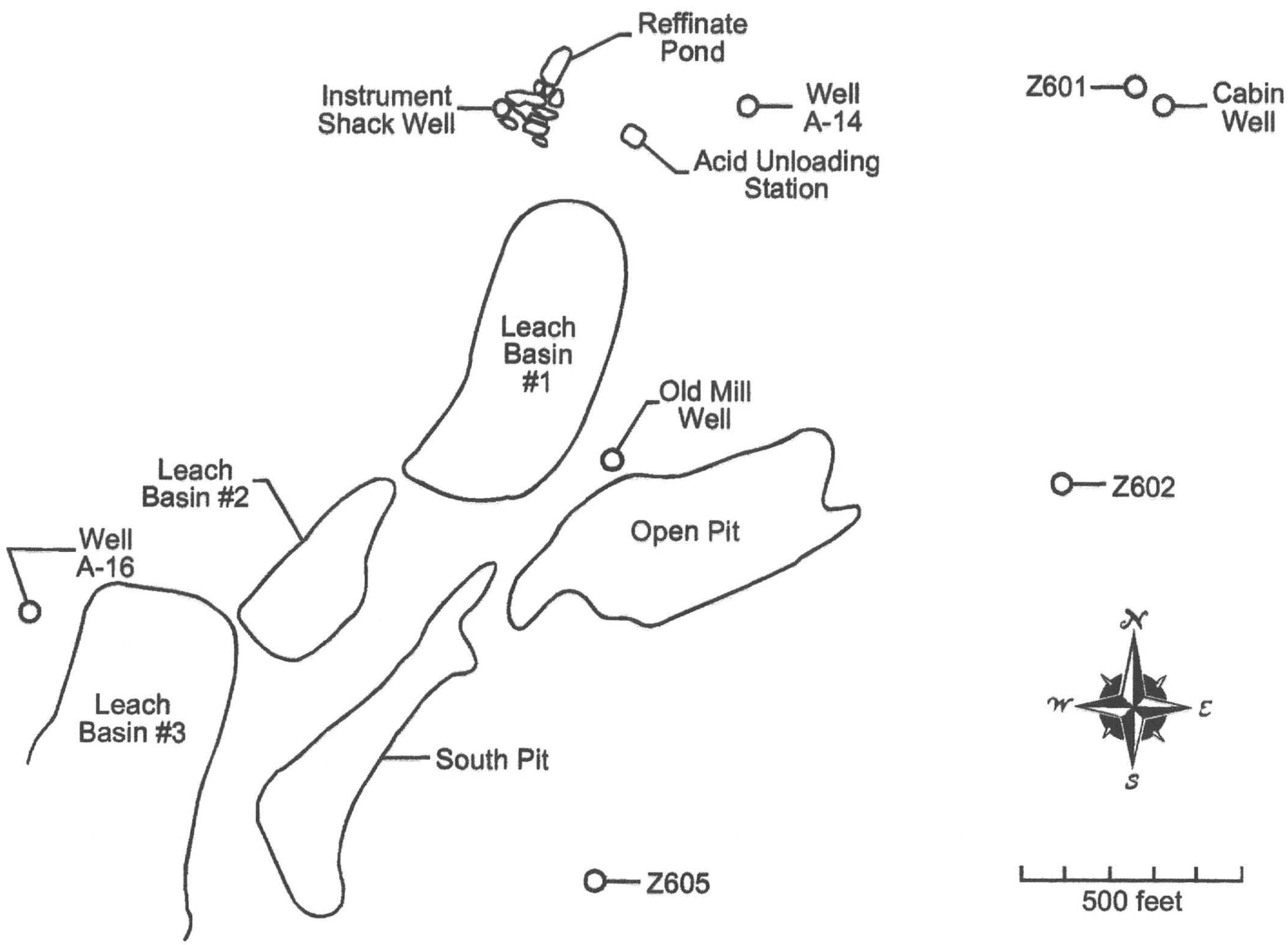

Figure 6-36. Site map for the Zonia Copper Mine.

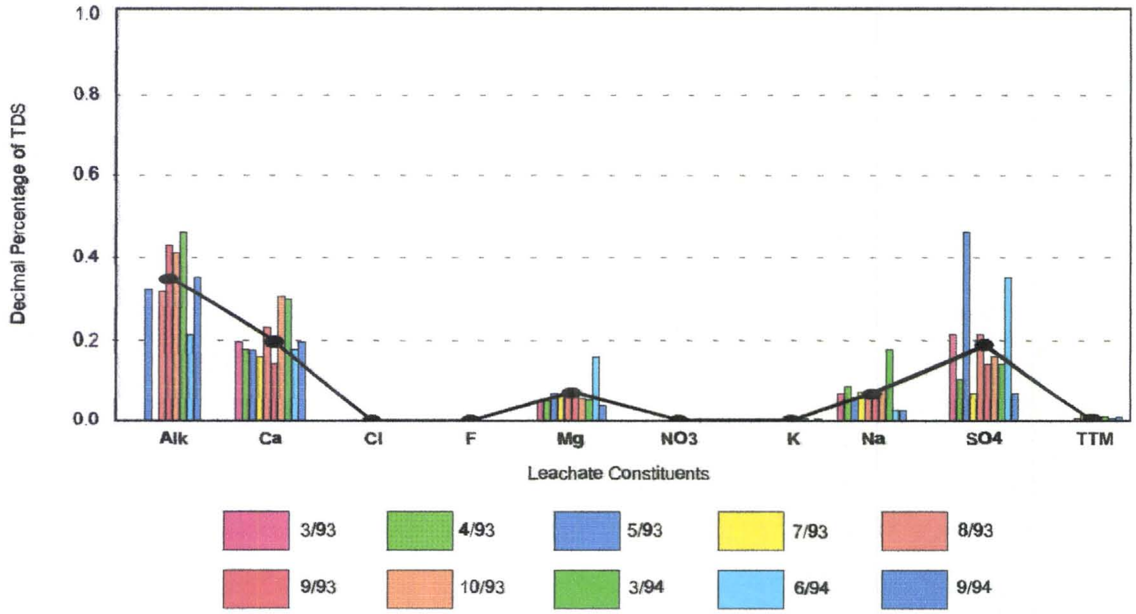

Figure 6-37. Geochemical fingerprint at upgradient Well A-16.

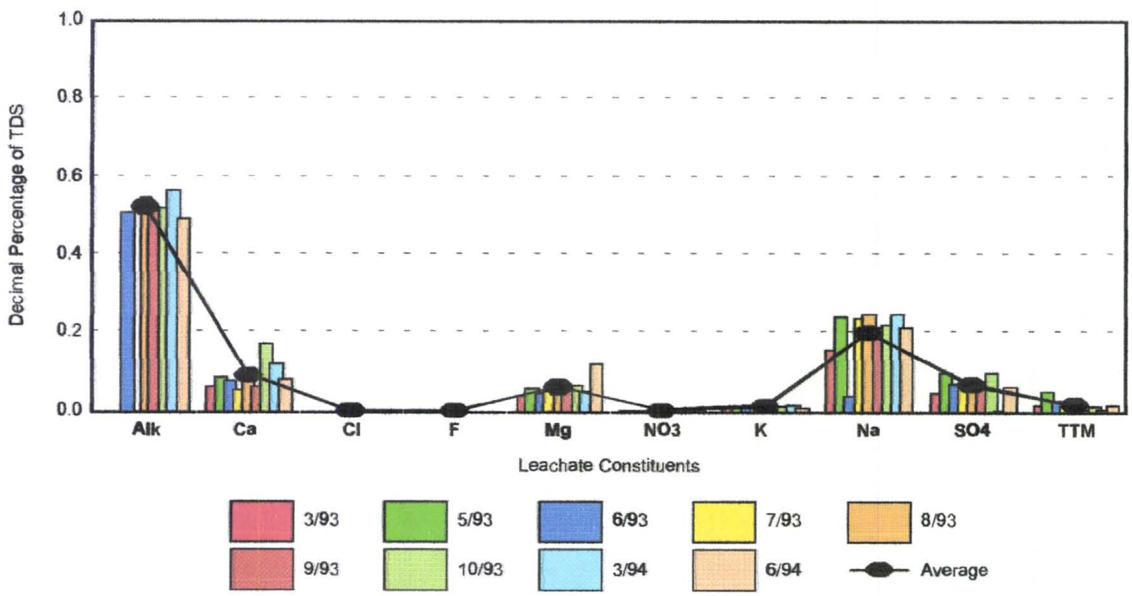

Figure 6-38. Geochemical fingerprint at downgradient Well Z601.

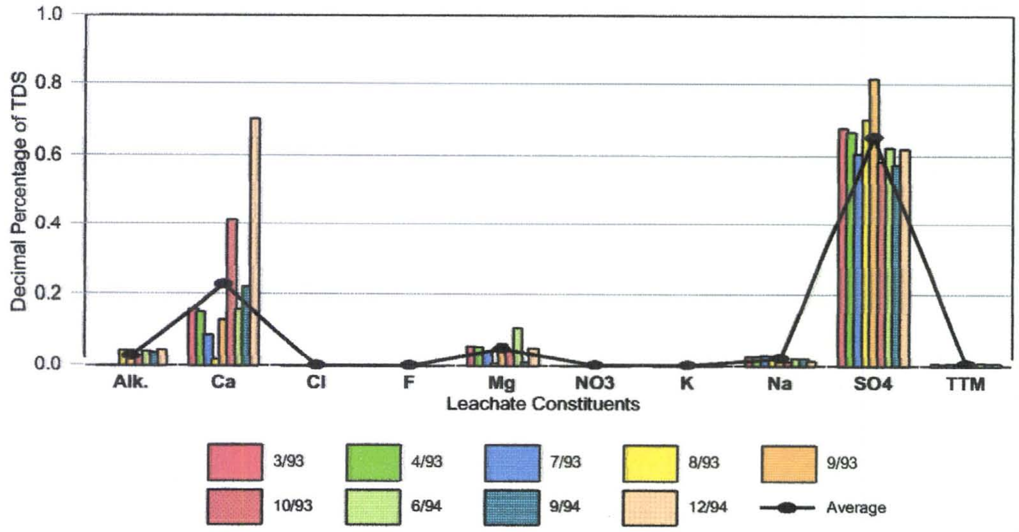

Figure 6-39. Geochemical monitoring results at the Old Mill well.

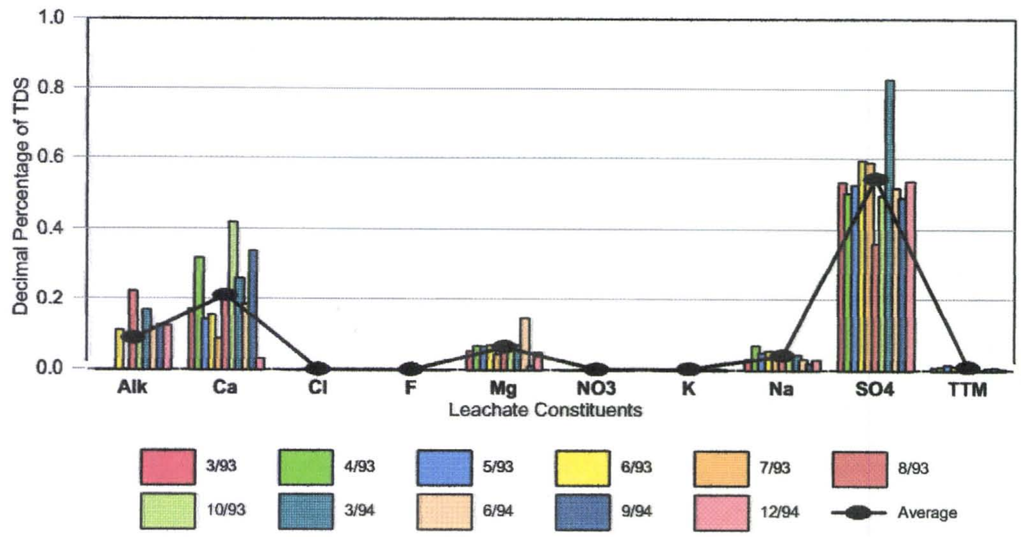

Figure 6-40. Geochemical monitoring results at Well A-14.

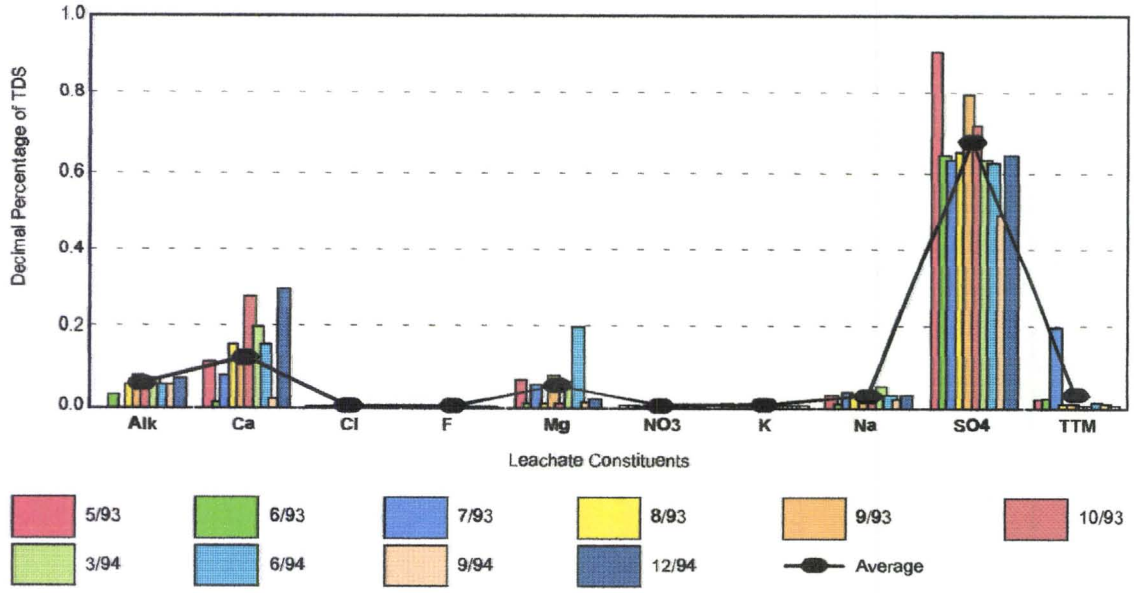

Figure 6-41. Geochemical monitoring results at Well Z605.

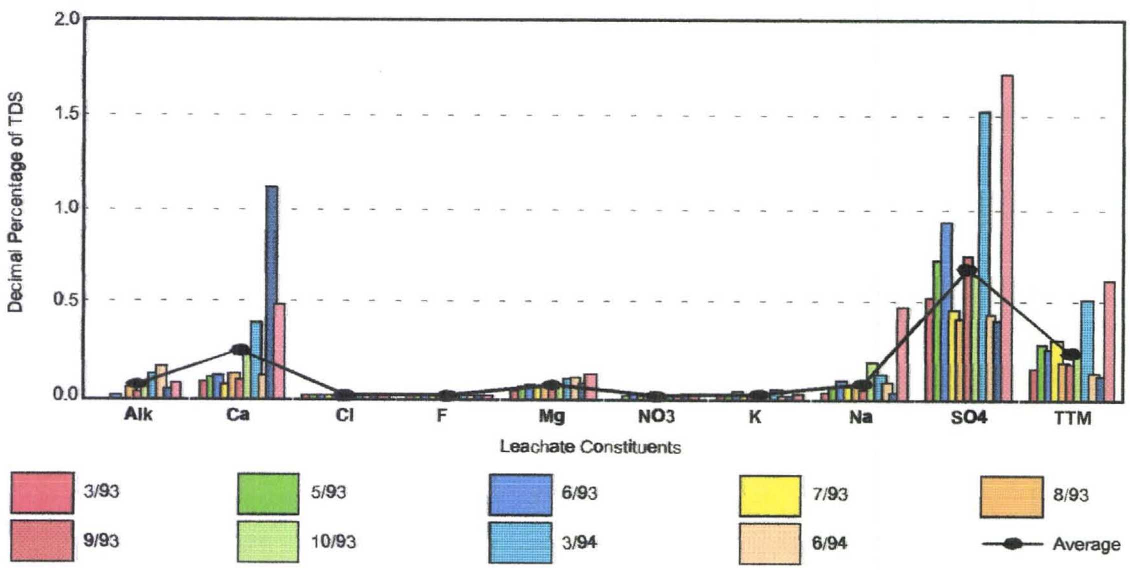

Figure 6-42. Geochemical monitoring results at Well Z603.

Table 6-8. Assessment of the ground-water monitoring results from the Zonia Copper Mine.

Location	Geochemical Pattern	TDS[1]	Reproducibility[2,3]		Upgradient Match[2,3]	
Well A-16	Alk-rich, SO_4-poor	300-800	76.3	(15)	—	
Well Z601	Alk-rich, SO_4-poor	300-500	94.0	(21)	74.2	(7)
Well Z607	Alk-rich, SO_4-poor	200-600	69.8	(15)	49.7	(6)
Cabin Well	Alk-rich, SO_4-poor	300-500	79.8	(6)	73.1	(4)
Cuprite Well	Alk-rich, SO_4-poor	200-300	94.0	(28)	94.4	(8)
Old Mill Well	SO_4-rich, Alk-poor	2800-3300	85.6	(36)	11.6	(9)
Instrument Shack	SO_4-rich, Alk-poor	1300-2300	83.9	(55)	20.9	(11)
Well A-14	SO_4-rich, Alk-poor	1800-3000	84.9	(55)	22.1	(11)
Well Z602	SO_4-rich, Alk-poor	1400-1900	91.1	(28)	24.5	(8)
Well Z603	SO_4-rich, Alk-poor	1000-4000	94.3	(6)	8.5	(4)
Well Z605	SO_4-rich, Alk-poor	1600-1900	93.1	(28)	12.7	(8)

[1] Total dissolved solids concentration expressed in mg/L.
[2] Listed value is the average regression analysis r^2 value times 100.
[3] Value in parenthesis is the number of regression analysis performed.

The same graphical fingerprinting technique that was used at ash monofills and heap leaching facilities was applied to the copper mine data. The concentration for each constituent was divided by the total dissolved solids concentration of the tailings leachate. This data normalization process reduced the effect of concentration variability between surveys and provided a rapid method to assess data quality. The resultant fingerprint patterns were compared visually and statistically using regression analysis.

The monitoring records for the individual copper mines did not contain results from multiple locations in a recirculating process solution as was the case with the heap leaching facilities. However, each mine generally contained several years of monitoring data for their tailings basin. These data were used to develop geochemical fingerprints for the tailings leachates and to evaluate their reproducibility over time.

1. The Twin Butte tailings leachate had a sulfate-rich, alkalinity-poor fingerprint. The reproducibility of this pattern during 14 surveys over 5 years was 97 percent.
2. Leachate in the Phelps-Dodge tailings disposal area had a sulfate-rich, alkalinity-poor geochemical fingerprint. Based on 10 quarterly surveys at six wells in the tailings disposal area, the reproducibility of the Phelps-Dodge fingerprint was 99 percent.
3. Tailings leachate at the Cyprus Sierrita Mine had a sulfate-rich, alkalinity-poor fingerprint. The reproducibility of this pattern based on sampling results from six locations in the tailings disposal area was estimated to be 88 percent.
4. The Zonia file did not contain any information on the tailings pond composition. However, ground-water monitoring results from several wells near the mill site produced geochemical fingerprints that were sulfate-rich and alkalinity-poor and had reproducibilities ranging from 83 to 86 percent. This pattern is very similar to the tailings leachate fingerprint observed at the Twin Butte, Phelps-Dodge, and Cyprus Sierrita copper mines.

At each of the copper mines, the geochemical monitoring results defined a consistent and reproducible pattern for the tailings leachate. However, unlike the heap leaching facilities, the geochemical fingerprint for copper tailings leachates was nearly identical at all sites. This was undoubtedly influenced by the fact that each mine uses a sulfuric acid based raffinate to extract copper from the ore being processed (sulfate is the dominant ion, leachate pH is approximately 2).

The next step in evaluating the composition of copper tailings leachates was to demonstrate that the identified tailings leachate fingerprints were different from background conditions at each mine. Since there was no information on make up water used at each of the copper mines, the tailings leachate fingerprints were compared to geochemical fingerprints for ground water upgradient of the mine. In each of the case studies, the upgradient ground water was characterized by relatively high levels of alkalinity (40 to 50 percent of the total dissolved solids concentration) and relatively low levels of sulfate (10 to 20 percent of the total dissolved solids concentration). The geochemical fingerprint for tailings leachate was visually and statistically distinct from the background fingerprint at each mine.

The final step in the site assessment was to contrast the tailings leachate fingerprint with the geochemical fingerprint in ground water downgradient of the tailings disposal areas. In each of the case studies, two distinctive geochemical fingerprints were present in the ground water downgradient of the tailings basins. One of the patterns was an alkalinity-rich, sulfate-poor fingerprint that was identical to conditions upgradient of the tailings basin. The similarity of these fingerprint indicates that mining activities have not had an impact on the ground water in these areas. However, the second pattern identified at downgradient monitoring locations was a sulfate-rich, alkalinity-poor fingerprint that was very similar to the tailings leachate fingerprint (85 to 99 percent match). These results clearly identify areas that have been impacted by fugitive tailings leachate.

The evaluation of monitoring records from the Arizona copper mines demonstrated that tailings leachates have a characteristic ionic fingerprint and this distinctive geochemical signature will retain its identity as the leachate migrates through the subsurface environment. Both of these properties of mine waste leachates were also observed at the Nevada heap leaching sites.

Although the primary objective of the data collection phase of the project was to obtain field monitoring results that could be used to characterize mine waste leachates and environmental conditions in the vicinity of mining operations, the individual site files were also reviewed for additional information on the composition or behavior of mine waste leachates. One very beneficial study recovered during the course of this project was a laboratory column study performed on behalf of the Twin Butte Mine. This particular study was initially performed to determine the attenuation coefficients of individual tailings leachate constituents. However, because complete sample analyses were performed, it was possible to use this study to evaluate the behavior of the tailings leachate fingerprint under controlled laboratory conditions.

The solution applied to the laboratory soil columns had a geochemical fingerprint that was identical to the Twin Butte tailings leachate. The initial eluant samples collected from the soil columns had geochemical fingerprints that produced a 90 percent match with the original leachate fingerprint. Subsequent eluant samples collected from the soil columns had a 95 to 99 percent match with the tailings leachate fingerprint. The results of this study demonstrate that the geochemical fingerprint will remain intact as tailings leachates migrate through a soil column. As a consequence, the geochemical fingerprint functions as an internal tracer that can be used to detect and identify tailings leachate at some distance from the source. This characteristic verifies the identification of tailings fingerprints at monitoring locations downgradient of each copper mine.

The Twin Butte column study was also useful for assessing the relative mobility of tailings leachate constituents. As discussed above and shown in Figure 6-43, the geochemical fingerprint transited the soil column immediately and with minimal distortion. However, the trace metals, that collectively represented 11.9 percent of the total dissolved solids concentration of the leachate applied to the column, were not present in the collected eluant samples. While it would have been interesting and informative if the column study had been run for a longer period of time, the results demonstrate that the trace metals in leachate will migrate more slowly than the individual geochemical parameters and the geochemical fingerprint.

The Twin Butte site monitoring data provided corroboration of the slower mobility of trace metals in tailings leachate. Specifically, the monitoring results for Well M-2 (Figure 6-16), Well 1225 (Figure 6-16), and Well M-7 (Figure 6-17) graphically depict tailings leachate migrating past these station. In each example, the ground water composition under went a systematic change from an alkalinity-rich, sulfate-poor fingerprint to a sulfate-rich, alkalinity-poor fingerprint that resembled the tailings leachate fingerprint. Even though trace metals represent more than five percent of the total dissolved solids concentration in leachate, trace metal increases were not detected at the monitoring stations before, during, or after the detection of the tailings leachate geochemical fingerprint. The significance of this observation is that monitoring for trace metals would not provide an early warning or detection of mine waste leachate migration because of their slower rate of movement.

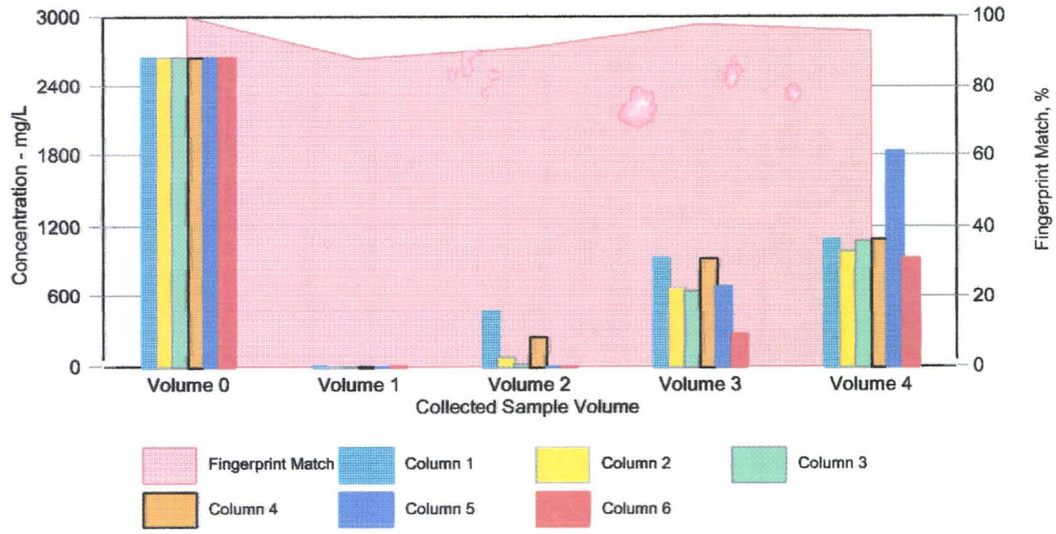

Figure 6-43. Comparative mobility of the geochemical fingerprint and trace metals in copper tailings leachate.

6.6 Arizona Copper Mines Summary

Site monitoring records from 4 copper mining operations in the State of Arizona were compiled to characterize tailings leachates. A review of this information showed that copper tailings leachates shared many of the compositional characteristic of process solutions and tailings leachates at heap leaching facilities. These specific properties included (1) the concentrations for individual constituents were highly variable, (2) the small subset of geochemical parameters were the most abundant constituents and represented more than 90 percent of the total dissolved solids, and (3) the geochemical parameters defined a multiple-ion chemical signature that uniquely fingerprinted the tailings leachate composition.

The case studies that were summarized demonstrated that the copper tailings leachate fingerprints displayed the following attributes:

1. The geochemical fingerprint at each mine was reproducible. Based on 2 to 5 years of monitoring results, the leachate at each mine had a consistent sulfate-rich, alkalinity-poor pattern. The reproducibility of the geochemical fingerprint ranged from 88 to 97 percent.
2. The tailings leachate fingerprint could be distinguished, both visually and by regression analysis, from the fingerprint of ground water upgradient of the tailings disposal area.
3. The fingerprint retained its chemical identity when leachate migrated away from the tailings disposal area. Thus, the geochemical fingerprint acts as an internal tracer to identify the leachate and areas impacted by the leachate.

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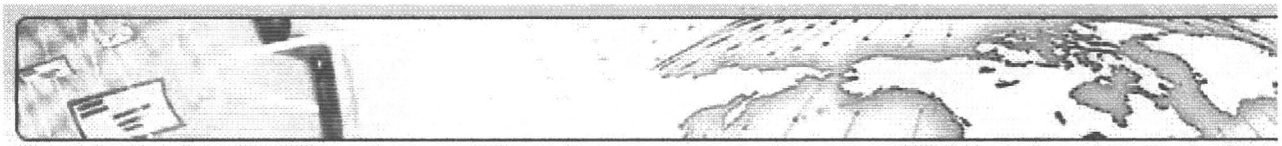

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