Hydrogeology of Molaoi Mining District (Lakonia - Greece)
By G. BOTTINO¹, M. CIVITA¹, L. MANZONE¹, G. OLIVERO¹, B. VIGNA¹

¹Dept. Georisorse e Territorio - Politecnico di Torino
C. so Duca degli Abruzzi, 24 - 10129 Torino - Italy

ABSTRACT

In order to enhance the Molaoi Mining District an hydrogeological study, aimed at evaluating possible interactions between groundwater and mining development, has been performed.

FOREWORD

Following on the stipulation of the convention "Molaoi Mining Project" between the European Economic Community (EEC), the Aegean Metallurgical Industries S.A. (METBA) and Institute of Geology and Mineral Exploration (IGME) of Athens and the POLITECNICO of Turin regarding Geomineralogical Studies for the Evaluation of the Mixed Sulphide Deposit of Molaoi, Greece, the Working Group for Hydrogeological Problems has developed a research on geological, structural and hydrogeological situation of the entire area of Molaoi.

The aim was to evaluate the possible interactions between groundwater and mining development, both in the perspective of a cost/benefit assessment and pointing out the most effective approach to exploitation and mining operations.

On the basis of the hydrogeological and hydrogeochemical data recorded, the hydrogeological model was thus identified. The evaluation of the behaviour of the system, of the delay time of the aquifer to rainfall and pumping has made it possible to characterize the Molaoi aquifer.

The study may provide indications for more detailed research on the preliminary project of a centralized dewatering plant and for drawing up management maps for mine exploitation.

GEOLOGICAL FEATURES

The morphology of the area is characterized by a wide valley and the thalweg occurs within the volcanic sequences.

4th International Mineral Water Association Congress, Ljubljana (Slovenia)-Pörschach (Austria), September 1991
The geology of Molaoi District \cite{1,2} is characterized by the presence of a thick Mesozoic sequence, made up of carbonated rocks (carbonated series of Tripolis Zone) resting unconformably upon a composite Paleozoic series (Tyros Beds), consisting of marbles, metaclastic sequences and a volcano-sedimentary serie, mainly consisting of tuffs and volcanic breccias.

At a higher level a clastic series (Upper Clastic Series) made up of more or less thick carbonate layers interbedded with calcarenites and shales is surveyed. Above and in conformity with these sequences there lies a volcanic series (Volcanic Metalliferous Series) consisting of interlayered tuffs of diverse nature (lapilli tuffs, cinerite tuffs, etc.), volcanic breccias and andesitic lava flows.

The entire volcanic sequence is crossed by cataclastic or mylonitic bands, locally associated with exploited mixed sulfide mineralization.

Early alluvial deposits widely outcrop in the southern zones of the area mainly with a sandy-pebbly composition and somewhat variable thickness (ranging from a few metres to several dozens of metres). These rest directly on the Paleozoic and Mesozoic sequences.

Structurally, the entire Paleozoic sequence is strongly folded and displaced by faults prevalently directed N50°W and N50°E. The volcano-sedimentary deposits are separated from the upper volcanic sequence, at a level corresponding to the intermediate clastic series, by an important dislocation oriented N-S and NW-SE and almost vertical dipping (Figure 1). As a result this discontinuity separates the carbonate and calcarenite deposits of this horizont, breaking them down into thin lensed and sometimes overthrust on the volcano-sedimentary series.

The Mesozoic sequence, which rest unconformably to the volcanic layers, in its turn is characterized by gentle folds and considerable fault systems.
HYDROGEOLOGICAL SKETCH OF MOLAOI MINING DISTRICT

HYDROGEOLOGICAL LEGEND

RELATIVE PERMEABILITY DEGREE

High Medium Low Imp

LATE ALLUVIAL COMPLEX
EARLY ALLUVIAL COMPLEX
UPPER CARBONATIC COMPLEX
VOLCANIC COMPLEX
ARENACEOUS - CARBONATIC COMPLEX
VOLCANO - SEDIMENTARY COMPLEX
METAPELITIC COMPLEX
LOWER CARBONATIC COMPLEX

SYMBOLS

FAULT AND TECTONIC CONTACT
PROBABLE FAULT
FLOW DIRECTION (ASSESSMENT)
PERMANENT SPRING
OBSERVATION WELL
MALAOI MINE - WORK

Figure 2: Hydrogeological sketch of Molaoi Mining District

4th International Mineral Water Association Congress, Ljubljana (Slovenia)-Portschach (Austria), September 1991

Reproduced from best available copy
Hydrogeological complexes

On the basis of their lithology and the type and degree of the relative permeability which characterize them, the various outcropping formations in this area may be subdivided into the following hydrogeological complexes, proceeding from top to bottom, according to their stratigraphic sequence (see the Hydrogeological Sketch enclosed - Figure 2):

- Late Alluvial Complex, made up of sandy-clayey deposits which emerge in main watercourse bed. Medium - low permeability - Aquitard;
- Early Alluvial Complex, consisting predominantly of carbonate pebbles, locally cemented, with scarce sandy matrix. Medium to high permeability, it plays a secondary hydrostructural role in the area of the mine - Aquifer;
- Upper Carbonatic Complex, consisting of limestones and dolomitic limestones with high permeability due to fracturing and karst. It is the main aquifer in the area (Carbonate Series of Tripolis);
- Volcanic Complex, characterized by various types of rocks with a permeability varying from low to medium degree - Aquitard (Volcanic Metalliferous Series);
- Arenaceous-carbonatic Complex, made up of limestones, calcarenites and shales in lenses broadly concordant with the general pattern of the volcanic complex. The carbonate lenses constitute limited intercalated aquifers with medium - low permeability (Upper Clastic Series);
- Volcano-sedimentary Complex, consisting of tuffs, characterized by a low secondary permeability - Aquitard;
- Metapelitic Complex, made up of fine grain-size very low permeable sequences. It often constitutes a permeability seal (3) stopping the groundwater flow within Palaeozoic marbles - Aquiclude (Lower Clastic Series);
- Lower Carbonatic Complex, made up of marbles (Marbles of Kurkula), medium-high permeability by fracturing and karst. Owing to the presence of intercalated impermeable levels (Metaclastic sequence) and various fault systems displacing it, the aquifer is somewhat compartmentalized.

Characteristics of the aquifer

The volcanic complexes described above are made up of rocks that differ from one another in lithology and fracturation. This entails a considerable variability of primary and secondary porosity which means an extreme variability of permeability values and groundwater flow conditions.

The various boreholes data show the existence of a general saturation level. Broadly speaking, it may be said that the piezometric surface trend generally follows the morphology of the area and is from 2 to 60 metres deep.

It is possible to recognize, especially in the volcano-sedimentary complex, a general flow direction toward E. In the volcanic complex, along the mineralized belt and its neighbouring areas, on the other hand, the groundwater flow direction tends to be considerably more complex owing to impermeable levels and fractured areas which subdivide the aquifer into semi-dependant reservoirs (5), becoming NW-SE. The groundwater outflow from the Paleozoic
Botino et al. - Hydrogeology of Molaoi, Greece

marbles, not supported by field evidence, cannot be altogether ruled out, in spite that this flow could be limited to very small areas.

Concerning the hydrodynamics of the volcanic complex, an extremely variable water-table trend might be envisaged by overall piezometric data \(^{(8,9)}\); areas with pronounced local gradients (for low-permeability areas) alternate with low gradients and gentler slopes water table ones.

The seasonal variations of the piezometric levels confirm the above said features of the volcanic complex. In fact, almost negligible variations are observed in the less permeable areas, whilst in other areas, values of about 30 m have been recorded.

A comparison with the seasonal rainfall records brings out for the majority of the wells, a slow and gradual rise in the piezometric level with delays, compared to the periods of higher rainfall, of about 20 days.

From a comparative examination of the piezometric diagrams, a somewhat similar general trend emerges for all the piezometers: a peak around the Spring period (Figure 2).

The aquifer shows lowest piezometric levels during the winter period, corresponding to the maximum rainfall. At the end of this period a gradual rise of the piezometric levels is observed, although in 1987 the rise was recorded on November. The same general trend can be found in the measurements of flow rates in the Molaoi mine.

Thus, it is possible to note a comparatively uniform behaviour on a large scale, but a less uniform one on a medium scale. Very close wells do not show the same responses to the infiltration, as in the case of those located in the central zone of the volcanic rocks, where fluctuations of 3 m and 30 m are observed in neighbouring wells. This behaviour is strongly affected by the presence of lithological and structural discontinuities, as has been already pointed out.

Figure 3: Piezometric levels in Volcano-sedimentary Complex and Volcanic Complex compared to precipitation data
The situation in the vicinity of the mineralized levels is rather complex because of the presence (both bottom and top) of mylonitic or cataclastic bands with metric thickness.

From the point of view of fracturing, the lavas are generally rather compact, the breccia rocks are moderately to highly fractured and the tuffs are moderately fractured, but with a high percentage of fine grain-size materials which fill up the larger fractures.

Owing to the differing degrees of fracturing, these structures may in turn constitute either impermeable strata or belts having a higher degree of permeability. Where mylonite and fine sediments prevail, there form permeability seals opposite to the groundwater flow. On the other hand, where the belts consist of cataclastic rock, it is possible to identify localized more pervious areas in which the water flow is directed and facilitated (conditions of preferential drainage). The water circulation, as has been noted directly in the mine pit, tends to follow preferential flow paths within cataclastic zones or recent and less filled fractures, with concentrated inrushes yielding 1-2 lpm. In the tuffs, even if scarcely fractured, a diffuse and poor yielding groundwater flow take place.

Using orientation data, it has been possible to distinguish four main systems of fracturing and by HOEK and BRAY's formula to calculate the permeability coefficient for various systems of discontinuity. K values, obtained by means of this method are given in Table 1.

Notwithstanding the fact that the values are only indicative because of the limited number of measurements and the considerable anisotropy, it is possible to note that the system N55°W, coaxial to the average mineralization trend, has the largest draining capacity. This is confirmed by the direct observations made in the mine.

On the basis of observed evidences, it is possible to confirm that, also in detail, the aquifer is comparted in several semi-dependent reservoirs and is characterized by an extreme complexity of piezometric surface with high and irregular hydraulic loads.

<table>
<thead>
<tr>
<th>System n.</th>
<th>Orientation</th>
<th>Spacing (cm)</th>
<th>Aperture (cm)</th>
<th>Permeability k (cmps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k 1</td>
<td>N25W/55SW</td>
<td>5.0</td>
<td>0.1</td>
<td>1.619</td>
</tr>
<tr>
<td>k 2</td>
<td>N75W/69NE</td>
<td>10.0</td>
<td>0.1</td>
<td>80.941</td>
</tr>
<tr>
<td>k 3</td>
<td>N55W/35SW</td>
<td>20.0</td>
<td>1.0</td>
<td>404.703</td>
</tr>
<tr>
<td>k 4</td>
<td>N74W/58SW</td>
<td>10.0</td>
<td>0.1</td>
<td>6.809</td>
</tr>
</tbody>
</table>

Table 1: Average characteristics of joint systems
WATER CHEMISTRY

Chemical analysis of Molaoi District waters, sampled during summer 1989, show that global mine waters (no. 1 and 2) are well balanced, while well and spring waters show marked percentage difference, revealing a lack of equilibrium of one or more dissolved ion pairs. Refering to their total mineralization, mine water samples show TDS values of about 1 g/l; all other sampled waters have a TDS value that ranges between 520 mg/l and 640 mg/l. Similar remarks can be done on water hardness evaluated in french degrees.

As regards the behaviour of single geochemical parameters, mine waters constantly present higher ionic concentration, but not always the highest values of single analyzed ions.

Piper’s diagram (Figure 4) puts in evidence, mainly in the rhombus diagram, a primary difference between mine waters (triangles) and all other waters (circles). The later belong to the family of Ca-Mg-bicarbonate waters, while the former seem to be a mixing between calcium-sulphate waters and Ca-Mg-bicarbonate waters. A further difference can be observed in the group of Ca-Mg-bicarbonate waters: well 5 and spring S2 (squares) are in fact weakly Ca-sulphate bearing. Moreover the cations triangle shows how bicarbonate waters are, as a matter of fact, greatly differentiated particularly as regards magnesium content.

Figure 4: PIPER’s diagram of Molaoi District sampled waters

Plotting data on Schoeller’s diagram (Figure 5) one can see that mine waters (samples 1 and 2, called group A1) are really a mixing of calcium-bicarbonate and calcium-sulphate waters, and that they can be easily distinguished from all other waters coming from Molaoi District. Samples 4, 5, 6 and 9 (group A2) show similar chemical composition, with a calcium-bicarbonate base mark, and little sulphate and nitrate content. In a similar way samples 7, 8 and 10 and the two springs (group A3) can be grouped, as they are mainly Ca-Mg-bicarbonate and their sulphate content is always higher than group A2, though it never reaches the values observed in group A1 waters.

We must remark also that, to the main chemical features attributed to each group, must be added a secondary mark that we could call Na-prevailing, due to the acid hydrolysis of volcanic rocks in the area.
Figure 5: SCHOELLER's diagrams showing chemical features of Molaoi District waters
In short, from analytic data and from Piper's and Schoeller's diagrams one can deduce that:

- mine waters (group A1, samples 1 and 2) are originated by a mixing between sulphate enriched waters, derived from the oxidation of ore deposits (sulphides) and Ca-Mg-bicarbonate waters circulating in Molaoi District aquifers;
- group A2 waters (samples 4, 5, 6 and 9) seem circulating in aquifers with a CaCO₃ matrix (and subordinate Mg), like the volcano sedimentary complex and show, as a consequence, calcium-bicarbonate features. Their scarce affinity with sulphate ion and the discrete nitrate content, reveal that they are not in direct connection with sulphide deposits;
- group A3 waters (samples 7, 8, 10, 11 and 12) are related with CaCO₃ and Ca, Mg (CO₃)₂ matrix aquifers, as a consequence of flow through altered andesites or basalts and show a good affinity with dissolved sulphate. This fact can be related with a partial dissolution (and re-oxidation) of sulphide from ore deposits in the volcanic formations; most waters of this group seem however to be affected by "mixing" between re-oxidation waters and calcium-bicarbonate waters, lacking in sulphate;
- water collected in 5 well (sample 3) do not fall within any group and could be roughly an "interface" between group A2 and group A3.

A different approach to the problem can be attempted by the analysis of some ionic rations, or better using a further and more sophisticated method of study (5), based on 6 new parameters, called briefly A-F; the six parameters are normalized between -100 and +100 and are weighted through the sums of cations and anions, in order to better understand the effect of each analyzed ion with respect to the TDS of sampled groundwaters.

The six parameters are plotted on rectangular diagrams (Figure 6) to put in evidence their great range of values. The hydrogeological and geochemical analysis of the parameters, confirms that mine waters are in relation with the reoxidation of ore sulphides in the volcanic sequence; moreover, a potassium enrichment in groundwaters, usually indicates an aquifer with prevailing volcanic rocks, or better a mixing between waters circulating in limestone formations and waters enriched in a Na and K because of base exchange with the rock host.

Most analyzed waters (samples 6, 7, 8, 10, 11; group B3) show a trend very similar to that of groundwater circulating in dolomitic-limestone sequence (with subordinate gypsum and anhydrite or oxidated sulphide ores).

Sample 3 is the only one whose diagram seems to be a typical groundwater circulating in volcanic rocks, enriched in potassium; it is likely to be a narrow aquifer inside the volcanic sequence, with reduced connections with all other aquifers in the area.

Mine waters (samples 1 and 2; group B1) show an atypical shape, due to the mixing between calcium-sulphate waters (60-70 %) and calcium and magnesium-bicarbonate waters (30-40 %).

Groundwaters no. 4, 5 and 9 (group B2) do not fall into any standard shape, because of the anomalous value of D parameter (indicating circulation in dolomitic formations).

Summing up the observations carried out we can say that:

- mine waters (samples 1 and 2) are undoubtedly the result of a mixing between calcium-sulphate waters (from oxidation of sulphides) and calcium and magnesium-bicarbonate waters;
- waters no. 7, 8, 10 and 11 (that is those common to A3 and B3 groups) are Ca-Mg bearing waters; they could be related with dolomitic limestone (or merely dolomitic) aquifers, but also with weathered andesites or basalts;
- waters 4, 5 and 9 (common to A2 and B2 groups) are related to carbonate aquifers (with subordinate dolomite), but their origin is to be found in the non-volcanic fraction of the volcano sedimentary complex. The low sulphate content indicates that they have no connection with sulphides oxidation which take place in the mining area.

Figure 6: Rectangular diagrams showing A - F parameters in Molaoi District waters

4th International Mineral Water Association Congress, Ljubljana (Slovenia)-Pörtschach (Austria), September 1991

Reproduced from best available copy
CONCLUSIONS

The identification of an hydrogeological model of Molaoi Mining Area was performed, according to which the aquifer is comparted in a series of semi-dependent reservoirs. This results in an extreme complexity and great variability of the hydraulic heads, with a local very high variability of hydraulic gradient.

Geochemical analyses on water samples show a general "mixing" of waters of different origin, while only one of the samples collected in the District has the peculiar features of a water flowing into K-volcanic rocks.

Owing to the particular structure, this phenomenon might assume a certain importance in the mining area, on account of the presence of aquiclude strata, such as the mylonitic bands and the mineralization itself.

The behaviour of the aquifer is moreover strongly influenced by various fracture systems with high frequency and aperture that determine conditions of preferential drainage. The combined action of drainage along these fractures and the increase in hydraulic loads due to the impermeable strata could create hazardous conditions connected to the possible high pressure inrushes. Inrushes, however, would exhaust quickly owing to the low transmissivity of the aquifer and its limited recharge. This situation highlights the need to proceed to more detailed studies before building up the exploitation plans. Indeed, such studies have the aim of drawing up a "risk map" that would prevent mining accidents possibly related to concentrated and massive inrushes of water into the mine (8).

ACKNOWLEDGEMENTS

The Authors thank Dr. J. Georgoulis of IGME for his valuable assistance during the research and the METBA.

REFERENCES