Los residuos mineros distribuidos sobre grandes áreas son importantes peligros para el medioambiente. La enorme superficie que ocupan proporciona acceso a la erosión incontrolable por el viento y la lluvia, la infiltración del agua y el intercambio de aire. La contaminación de la materia gaseosa, disuelta, coloidal, particulada e incluso orgánica afecta a zonas pequeñas o, en el peor de los casos, a enormous áreas, dependiendo del tamaño de grano, modo de deposición y forma del material depositado. Centrándonos en el estudio de los procesos que tienen lugar dentro del propio material acumulado, es necesario un conocimiento básico respecto a la historia de deposición, roca madre, morfología, clima y vegetación. Es crucial elucidar el estrato quño del residuo minero depositado – su química, mineralogía, tamaño de grano, laminación, conductividad hidráulica, modelo de drenaje, química de las soluciones, actividad microbiológica, la relación ácido-base, los frentes de reacción y la formación de hardpan. La interacción de todos los parámetros controla el impacto medioambiental en un cierto intervalo de tiempo así como para toda la vida de una escombrera. La atenuación natural de contaminantes puede ser observada en el origen, a lo largo del camino del drenaje, así como debido a la mezcla y dilución con aguas no contaminadas. Un número de aspectos parecen ser relevantes para los procesos de atenuación en el origen. Basado en información del fondo químico, el peor escenario puede ser modelado. Esto puede ser modificado por el potencial de neutralización del propio material a corto y largo plazo. Teniendo en cuenta parámetros adicionales tales como la distribución del tamaño de grano, laminación, conductividad hidráulica, accesibilidad de fases reactivas, superficie específica expuesta y la morfología de la escombrera, podría hacerse una extrapolación del avance del frente de alteración así como del desarrollo de drenaje ácido de minas a largo plazo. Debido a que la mayoría de las escombreras no son monitoreadas para su impacto medioambiental, la información obtenida sólo proporciona datos de un segmento de tiempo. Un aspecto, que difícilmente puede ser incorporado a los modelos, es la reorganización interna de una escombrera. Después de la deposición, una escombrera sufre reorganización específica debido a procesos inducidos por meteorización y diagénesis, que básicamente afectan a los caminos del agua. En el marco de reorganización, el aumento del contraste físico-químico actúa como una capa límite que separa las porciones de las escombreras accesibles y alteradas, de las que están protegidas e inalteradas. Desafortunadamente, sólo en casos extremadamente raros, una cuantificación del balance de agua puede ser realizada debido a la pérdida de información básica sobre la precipitación, evaporación, retención, mineral incorporación o drenaje a ríos o aguas subterráneas.

Acid Mine Drainage Remediation Starts at the Source

INTRODUCTION

Mining residues are in general characterized by area consumption. Medieval mining was focussed on high grade ore generally associated to veins and shears - consequently, minimal waste rock, low grade ore, and fines were produced. In general, the waste material was deposited close to the adits, on slopes and into valleys, or was used for buildings, roads or to stabilize the mining area. Area consumption was minimal with locally high degree of contamination potential.

With changing mining technologies from high to low grade, but high tonnage and modified treatment techniques, enormous volumes of waste rock and treatment residues and slags were produced. This changed the morphology of the country side significantly. The distribution of mining residues over tens of square kilometres makes long term remediation almost impossible (e.g. lignite mining in Germany; porphyry cop-

**palabras clave:** Drenaje ácido de mina, atenuación natural, hardpan, estructura interna, contaminantes

**key words:** Acid mine drainage, natural attenuation, hardpan, internal structure, contaminants

Conferencia invitada: Rammlmair et al., Macla 10 (2008) 29-33

*corresponding author: rammlmair@bgr.de*
per mines in Chile, Iberian Pyrite Belt, Spain).

Mining residues have been in the environmental focus for several decades. Most detailed investigation focussed on the processes generating acid mine drainage (AMD), on the estimation of the worst case scenario. This scenario is modified by the short and long time buffering capacity of the gangue minerals, by changing accessibility of acid producing phases due to precipitating crystalline and amorphous secondary phases clogging pores and forming occasionally hardpans, by accumulation of heavy metals in storage minerals in the heap and along the drainage path. Finally dilution of the contaminants by mixing with uncontaminated rivers or groundwater (Fig. 1).

Natural Attenuation Potential

Potential contaminant
- Neutralization potential = “Worst case Scenario”
- Fixation in and on the heap
- Accessiblility over time
- Dilution by uncontaminated water
- Attenuation along the drainage path
- Final release to the environment
- AMD (over lifetime)

Investigation of mining residues is an extremely complex issue, since little is documented about the process of deposition, the material deposited, the treatment etc.. Deciphering of the depositional history and the processes taking place, requires intensive investigation on site and in the laboratory.

The aim of this paper is to show how natural attenuation is affected by structural reorganization, and the possible influence by acid mine drainage.

RESULTS AND DISCUSSION

Depositional history

The depositional history of mining residues rarely can be followed up in detail. Besides accessible information for recently active mines provided by mining companies or by former employees of the mine, little data exist about historical mine sites. Some information is provided by aerial photograph time series, which, however, generally do not cover the whole depositional history. Detailed reconstruction of the depositional process regarding changes of the material itself as well as the mode of deposition of the material with consequent fractionation of grains and minerals (Fig. 2) is needed for further investigation.

Both unsorted blocky materials with limited amounts of fines as well as slimes, contribute to AMD. The amount of contaminants mobilized and removed from the source can vary enormously even when the material and climatic premises fall into the same range. The mode of deposition plays a key role. Homogeneously deposited material often provides better access to fluids compared to chaotically deposited or layered material (Rammlmair, 2002). Sorting in the course of deposition of the material might be responsible for reactive mineral enrichment in layers, forming quasi impermeable thin layers due to alteration and subsequent clogging of pores by substantial amounts of secondary amorphous and crystalline phases.

Another crucial point is the depositional slope. Steep flanks contrast with sub-horizontal tops. Flanks are often subject to severe erosion, contributing fines to the rivers and, therefore, contaminating the river itself. On the other hand, even small morphological expressions at the sub-horizontal top might cause focussed water transport, due to a reduced infiltration capacity. The stability of some tailings dams is based on this sub-horizontal drainage. Blocky heaps are open to infiltration. To inhibit rain water infiltration fines have to lock the mega pore system to enhance the water retention capacity and enable horizontal rerouting (Fig. 3).

Natural attenuation

Natural attenuation is a welcome attribute to large sources of contamination, since remediation efforts would be enormous. Natural attenuation takes advantage of all available ingredients, to achieve equilibrium with the surroundings. Since materials from the mining industry provide enhanced surface areas and good accessibility, processes taking place within this material are much faster than similar processes taking place over thousands of years in the source rock, e.g. gossan formations. Within the treated material, accessibility is optimized due to grain size reduction. Therefore, high amounts of dissolved material are made available to the environment within a short time period. This is the source of AMD with high loads of contaminants, which is related to the immediate availability of the reacting phases.

Taking into account the volume of source material and the contaminants, enormous amounts of eventually toxic compounds would be released.

The interactions at the gas-fluid-rock interfaces and the kinetics of the processes taking place at these interfaces have a major influence on the dissolution, absorption, reaction, and precipitation processes taking place. Contrasting micro-environments might even enhance these processes.
Carbonates and some aluminosilicates such as biotite, hornblende and plagioclase are able to neutralize part of the acidity released due to oxidation of sulfides, and Fe(II) to Fe(III) transformation. Besides K, Ca, Al, Si and other elements go into solution, and even getting pH-conditions normalized, the load of Al, Si could get enhanced. Precipitation of gypsum, jarosite, goethite and of gels of highly variable compositions might occur.

The system “heap” shows a number of extremes and transitions. At zones of defined physical contrasts, such as saturated/unsaturated zones, pH, redox, T, and gas composition might show significant differences. Loss of water due to evaporation, changing pH conditions or mixing of fluids, might result in precipitation of secondary phases and a collapse of colloids to gels.

Some positions in the heap favour these dramatic changes. The most significant changes can be observed at the capillary fringe, were oxidation is prominent, and capillary driven transport with hyper-saturated fluids provides the environment for precipitating phases and gels due to evaporation. At an oscillating redox front at the boundary saturated/unsaturated zone, e.g. in a tailings system, cementation could lock the pores forming thin consolidated layers (Graupner et al., 2007). Similar, but probably less pronounced contrasts could be found at capillary barriers, at transitions between matrix and macro pore channels.

**Internal reorganization**

The effect of the physical changes taking place in the heap is twofold. On the one hand, high amounts of contaminants could be absorbed, precipitated and fixed in secondary amorphous and crystalline phases. On the other hand, the volumetric growth of hydrated phases locks up pores and agglutinates particles. These changes have major effects on the erosion, water migration, and air exchange. Due to the inhibition of infiltration by, horizontal rerouting, focused transport occurs on the surface or through the heap. Zones of the heap will be partially or even totally withdrawn from direct accessibility, and therefore from further reaction. The size of such cells varies from cm to hundreds of meters in diameter. The development of such cells is a continuous process, lasting a few to hundreds of years depending on the local premises. It is the most effective natural remediation measure, since the directly accessible source might be reduced by more then 50% (Rammilma, 2002; Rammilma et al., 2008). Unfortunately, a direct approval is not easy to be made.

Few geophysical methods can be applied to obtain information on the heap internal structure. Single shot electrical resistivity profiles provide ambiguous information. The interaction of water content, ion concentration, conductive minerals, grain size, and porosity makes interpretation of the results difficult.

Tomographic information can be obtained by parallel profiles, which outline bodies of the same resistivity range, and provide information on the bedrock morphology and eventually watersheds. In combination with surface observations, one can derive zones of material related resistivities (pyrite rich tuffs, gossan, slate).

Using differential imaging of geoelectrical resistivity measurements prior and after rainfalls helps understanding water migration within the heap (Grissemann et al., 2007; Rammilma et al., 2008).

Fixation of contaminants on surfaces of primary and secondary phases, in amorphous and crystalline storage minerals, and within plants is a common observed feature. The duration of the fixation is much dependent on the desorption ability, the solubility of the phases, the stability under changing pH-conditions, the accessibility of even soluble phases due to reduced porosity or enhanced water retention in the uppermost layers.

Besides the materials chemical, physical, and mineralogical background, the climatic influence has to be considered. Another critical aspect is the mineral and grain size fractionation during deposition of the material. This can cause preferential pathways, capillary barriers, or even critical enrichment of reactive phases being responsible for the development of hardpans and cemented layers (Graupner et al., 2007).

**Acid mine drainage**

The head waters of the Rio Tinto (Spain) consist of a number of small creeks. Besides pH-neutral waters and a natural contribution of acid mine drainage, the basic source of the river is low pH seepage draining the valleys filled with mining residues. This seepage contains substantial amounts of contaminants, such as Fe, As, S, Pb, Ba, Mo, Cu, and Al. The chemical load and the pH of the seepage water is much dependent on the deposited source rock type, the water retention capacity of fines in the heap’s interior, the sampling season, and the sampling point (Romero Baena, 2005.).

Basically, five rock types were deposited in heap slope parallel sheets, namely slate, gossan, pyrite ashes, pyrite poor and rich rhyolitic tuffs. The
central part, dominated by gossan and slate is surrounded by rhyolitic tuffs, which are in part highly enriched in pyrite.

Since the drainage system of the investigated heaps is influenced by a number of factors such as horizontal drainage, slope erosion and sinkholes, drainage areas do not correspond to the natural watershed system. (Fig 4) (Rammlmair et al. 2008).

Drainage path

Along the drainage path within and outside the heap, a number of physicochemical changes occur. Potential contaminants might absorb on crystalline and amorphous mineral surfaces or coagulate as colloids or precipitate as gels or individual crystalline phases. Changing Redox condition, pH, temperature drop, O2, bacteria, and evaporation might cause this. Seepage from mining dumps undergoes significant seasonal changes. Besides the changes in quantity, quality and load regarding the fast drainage after rainfall related to macro pore systems and the even in the dry season persistent slow matrix flow (Romero Baena, 2005), changes can be observed along the drainage path, too. Unfortunately reactions within the heap cannot be monitored, but locally attributed to changes in the source, from dominantly slate, gossan or pyritic tuffs (Rammlmair et al, 2008). The physicochemical premises of the seepage are influenced by oxygen availability via air, enhanced by cascades based on the river bed morphology, by temperature decrease or increase depending on the season, by reaction with and absorption by minerals of the riverbed, by colloid formation, coagulation and precipitation of amorphous FeH-films. The dissolved ions and the pH might show significant changes.

Most of the analyzed waters of Peña del Hierro show hyper-saturation of goethite in the course of oxidation, protons will be liberated when goethite precipitates. Other phases which would precipitate are small amounts of gypsum, anglesite and SiO2 (am). Critical for the pH-changes is the kinetics of Fe(II)-oxidation (tendency: pH increase), the precipitation kinetics of iron oxyhydroxides and jarosite (tendency: pH decrease), and the kinetics of minerals from the riverbed (tendency: pH increase).

The observed slight increase in pH along the seepage D over some 100 meters, with significant drop in conductivity and temperature (Fig.5) can be modelled on the base of Fe(II) oxidation.

![Fig 5](image5.png)

The outflow “D” shows significant changes of conductivity, redox, pH, oxygen, temperature, and morphology along a 110 m profile. The loss of temperature, conductivity and the increase in pH and oxygen is significant.

![Fig 6](image6.png)

Geochemical modelling of ionic strength and pH for oxidation of Fe(II) only, and combined with precipitation of amorphous Fe-phases. The model in part explains the development of Fig.5.
to Fe(III) and by precipitation of small amounts of goethite or jarosite (Fig.6).

Some of the seepage mixes with non-contaminated waters of near neutral pH. Dilution occurs according to the mixing ratio, but additionally some contaminants will instantaneously flocculate changing clear brown waters into turbid yellowish for some distance. The particles might float or settle on the river bank.

CONCLUSION

To estimate the acid mine drainage potential of a heap, it is basic to characterize the status quo of a heap according to the morphology of the heap itself, the bedrock, the material deposited, the mode of deposition, the internal structure, and the local climatic conditions. Unfortunately, there are few means to obtain information of the interior of a heap. Long term electrical resistivity measurements provide a good insight into structure and eventually water migration pathways. The information is not unambiguous, since water saturation and ionic strength interact. Additional information has to be obtained by independent chemical or physical methods, which in general cannot be applied in the field, but at a laboratory scale.

A number of factors influence the development of acid mine drainage directly at the source and along the pathway. Besides the neutralization potential based on the chemistry of the minerals, the long term availability and the amount of reactants during the process of weathering are crucial for the quantity of water getting access to the reactive phases and for the quality of the outflow. Reduction of the accessibility of the material and limiting the amount of water and oxygen infiltration, will have the strongest influence on AMD generation. Besides technical remediation efforts, natural processes such as clogging of pores, formation of hardpans or cemented layers, and generation of capillary barriers on the basis of grain size contrasts, are most effective to withdraw cells of the heap from further weathering. These natural processes develop over a number of years, much dependent on the material premises and the climatic conditions. Even if the processes are highly effective in limiting the size of the source, AMD does not stop immediately, but would change in quality and quantity over time. At this point, it is crucial to quantify the water household of a heap. The attempt to quantify it is in general hindered by incomplete sets of data.

Water that enters the source reacts with the material, leaches primary and secondary soluble phases. Part of the water will form hydrous compounds, part migrates down the heap, part will evaporate and precipitate into soluble and insoluble phases close to the surface (e.g. hardpans). The seepage leaching the heap after a rainfall might show a peak both in concentration and water quantity at beginning turning into a reduced rate after hours. The high concentration of contaminants is based on the immediate availability of highly soluble secondary phases, accessible pore water and macro pore channel system. Each rainfall after a dry period generates a first flush of elevated load of dissolved compounds. The intensity of the first flushes might change over time due to wash out of highly soluble effluorescent phases. It is therefore important to characterize the outflow, and to monitor seepage over a time period to differentiate between first flushes and background seepage. Unfortunately this is not easily performed, but is besides the geophysical investigation the only non-destructive access to the heap interiors.

Natural attenuation is hardly to be quantified, since the interacting processes last several years. On the other hand decision support pro or contra remediation activities is expected within a short time period. Some solution can be provided by modelling. Based on field observations and laboratory tests, relevant parameters can be obtained which can feed reactive transport models to predict the heap behaviour within the next hundreds of years.

ACKNOWLEDGEMENTS

The investigation was part of a project on hardpan formation on mining residua financed by the German Federal Ministry for Education and Research (BMBF) under the project FKZ 0330523. Thanks to the Director José María Mantecón Jara, of the Fundación Rio Tinto, for the support of the field work on their property.

REFERENCES


Dilution occurs according to the mixing ratio, but additionally some contaminants will instantaneously flocculate changing clear brown waters into turbid yellowish for some distance. The particles might float or settle on the river bank.

CONCLUSION

To estimate the acid mine drainage potential of a heap, it is basic to characterize the status quo of a heap according to the morphology of the heap itself, the bedrock, the material deposited, the mode of deposition, the internal structure, and the local climatic conditions. Unfortunately, there are few means to obtain information of the interior of a heap. Long term electrical resistivity measurements provide a good insight into structure and eventually water migration pathways. The information is not unambiguous, since water saturation and ionic strength interact. Additional information has to be obtained by independent chemical or physical methods, which in general cannot be applied in the field, but at a laboratory scale.

A number of factors influence the development of acid mine drainage directly at the source and along the pathway. Besides the neutralization potential based on the chemistry of the minerals, the long term availability and the amount of reactants during the process of weathering are crucial for the quantity of water getting access to the reactive phases and for the quality of the outflow. Reduction of the accessibility of the material and limiting the amount of water and oxygen infiltration, will have the strongest influence on AMD generation. Besides technical remediation efforts, natural processes such as clogging of pores, formation of hardpans or cemented layers, and generation of capillary barriers on the basis of grain size contrasts, are most effective to withdraw cells of the heap from further weathering. These natural processes develop over a number of years, much dependent on the material premises and the climatic conditions. Even if the processes are highly effective in limiting the size of the source, AMD does not stop immediately, but would change in quality and quantity over time. At this point, it is crucial to quantify the water household of a heap. The attempt to quantify it is in general hindered by incomplete sets of data.

Water that enters the source reacts with the material, leaches primary and secondary soluble phases. Part of the water will form hydrous compounds, part migrates down the heap, part will evaporate and precipitate into soluble and insoluble phases close to the surface (e.g. hardpans). The seepage leaching the heap after a rainfall might show a peak both in concentration and water quantity at beginning turning into a reduced rate after hours. The high concentration of contaminants is based on the immediate availability of highly soluble secondary phases, accessible pore water and macro pore channel system. Each rainfall after a dry period generates a first flush of elevated load of dissolved compounds. The intensity of the first flushes might change over time due to wash out of highly soluble effluorescent phases. It is therefore important to characterize the outflow, and to monitor seepage over a time period to differentiate between first flushes and background seepage. Unfortunately this is not easily performed, but is besides the geophysical investigation the only non-destructive access to the heap interiors.

Natural attenuation is hardly to be quantified, since the interacting processes last several years. On the other hand decision support pro or contra remediation activities is expected within a short time period. Some solution can be provided by modelling. Based on field observations and laboratory tests, relevant parameters can be obtained which can feed reactive transport models to predict the heap behaviour within the next hundreds of years.

ACKNOWLEDGEMENTS

The investigation was part of a project on hardpan formation on mining residua financed by the German Federal Ministry for Education and Research (BMBF) under the project FKZ 0330523. Thanks to the Director José María Mantecón Jara, of the Fundación Rio Tinto, for the support of the field work on their property.

REFERENCES