# Environmental geology of mining

## An example from a shale processing industry

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# ENVIRONMENTAL GEOLOGY OF MINING -
## AN EXAMPLE FROM A SHALE PROCESSING INDUSTRY

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# 1. ABSTRACT

I have studied the environmental pollution caused by an alum-factory based on the processing of black shales. The industry was abandoned in 1912 after 275 years of activity.

The present environmental problem is mainly water pollution caused by weathering of the shale spoils. The effluents contain less heavy metals than expected because there are geochemical barriers within the area.

It has been possible to obtain quite good information of the environmental pollution during the hey-day of the industry 200 years ago. The natural concentration of sulphate in the river was trebled and the buffering capacity of the river was strained but not surpassed. The worst pollution was caused by the dumping of shale residues into the river. The sediment transport of the river was increased 40 times.

The river has recovered from earlier environmental stress and is now one of the cleanest rivers in this part of Sweden. The reasons for this complete recovery are discussed.

*Environmental geology, heavy metals, mining, water pollution, black shales, industrial archeology, acid mine drainage.*

## 2. INTRODUCTION

Black shale is a rock which is gaining importance as a source of both metals and energy. Huge tonnages must be processed as the shale is a lean ore. In Sweden, plans have been advanced to mine 7 million tons a year to produce some thousand tons of uranium. In USA there are plans to mine 500 million tons of shale a year from the Green River Formation to produce oil.

Huge amounts of shale residues must be disposed of. Weathering of the shale residues can give rise to serious water pollution.

I have studied the environmental geology of an abandoned shale-processing industry at Andrarum, Skåne, Southern Sweden. The surrounding area is not affected by industrial pollution and the effects of the shale industry could be studied without interferences.

Even a rather superficial inspection of Andrarum reveals the effects of the weathering of the shale. Brown and yellow precipitates of iron are found in all the water-courses in the mining area.

My intention with this investigation was to gain a better understanding of some of the environmental effects of mining, particularly weathering of mine spoils

## 3. THE HISTORY OF THE ALUM INDUSTRY

Alum was formerly a substance of great economic importance (Singer 1948). It was used for dyeing, paper-making and tanning. At the beginning of the 19th century there were 10 alum factories in Sweden (Stoltz 1934). All were based on the leaching of alum shale. Andrarum was one of the largest factories.

The shale was mined, broken, burnt, leached and then disposed of. Figure 1 is an illustration from Agricolas book De re metallica (1556) and shows a procedure, which was used with some modifications in Andrarum.

The alum factory in Andrarum was in activity from 1637 to 1912, that is 275 years. During that period about 2 million tons of shale were processed (Stoltz 1932, Carserud 1978).

Andrarum is a small village in the south-eastern part of Skåne, Southern Sweden. The effluents from the alum industry are dumped into the river Verkeån.

Fig. 1 From Agricola *De re metallica*, Basel, 1556. A, Furnace; B, Heap of calcined ore for irrigation; C, Aluminous ore; D, Ladle for irrigation; E, Cauldron; F, Gutter, G, Trough.

## 4. CHEMICAL COMPOSITION OF THE ALUM SHALE

Alum shale occurs in many parts of Sweden. The geochemical composition of the shale from Västergötland is well known (Armands 1972). The shale contains many heavy metals in concentrations above the average rock, notably uranium with about 300 ppm in comparison to the crustal average of about 3 ppm.

The chemical composition of the shale in Southern Sweden has received less attention and for this reason I have undertaken a geochemical and mineralogical study on 10 samples of this shale (Carserud 1982b). Proton Induced X-ray Emission (PIXE) was used for the geochemical analysis of the trace elements. It is a new analytical method, of which I had to evaluate the advantages and drawbacks.

The shale is a very fine-grained rock, which limits the application of many standard methods for mineral analysis. The mineralogy of the shale was analysed with X-ray diffraction.

I have studied the correlations between minerals and elements with statistical methods. The results showed that illite is correlated with Na, Al, Si, K, Ti, Rb and Zr, Quartz is correlated with Si, Ti, Se and Mo, feldspar with Al, Si, K and Ti. Pyrite is correlated with Fe, S, P, Cu, Zn, As, Y and U. The elements Ca, Mg, Mn, Ni, Cu, Zn and Y are correlated with calcite while V, Se and Mo are associated with the organic matter.

A statistical correlation is only an indication that an element might be incorporated into a certain mineral. Elements and minerals can be statistically correlated without any direct association.

The correlations between elements and minerals have been used in conjunction with other data to evaluate the mobilities of elements in the weathering of the spoils

# 5. ENVIRONMENTAL POLLUTION AT PRESENT

## 5.1 REGIONAL ECOLOGICAL EFFECTS OF EFFLUENTS FROM ANDRARUM

The river Verkeån, into which the effluents from the alum-factory at Andrarum are emptied, is one of the cleanest rivers in Skåne. This is remarkable in view of the expected environmental deterioration due to the shale-mining.

Trout spawn in the river, some return to the sea and some are stationary (Anheden 1967). Other fishes in the river indicating clean water are bullhead *Cattus gobio* , minnow *Phoxinus phoxinus* and lampern *Lampetra planeri* (Andréasson 1967).

Fish-kills have occurred in the river. They have been caused by farmers emptying their sewage tanks and bear no relation to the weathering shales.

The algae of the river have been studied during several years. No effect of the effluents from the alum works has been traced (Amelie Fritzon, Lund, pers. comm.).

## 5.2 REGIONAL VARIATIONS IN GEOCHEMISTRY OF THE RIVER VERKEÅN

Applications of geochemistry in mineral exploration are well established. They can also be used in pollution studies. The degree and extent of water contamination in some parts of the United Kingdom have been studied by geochemical techniques (Thornton 1975).

The environmental pollution from Andrarum seemed to be rather inconspicuous. Recent sediments deposited downstream from Andrarum, however, had high concentrations of many heavy metals (Carserud 1978). This could be evidence of an environmental pollution but it could also be caused by a reworking of old inert sediments.

I investigated this water contamination by sampling stream water in different parts of the drainage basin. The analysis of dissolved and suspended heavy metals in the stream water showed large natural variations (Carserud 1982a). Areas with shale in the bedrock gave a run-off with higher concentrations of heavy metals than other areas. The influence of pollution from Andrarum could not be traced with these samples.

I believe that this is due to the slight environmental stress caused presently by the effluents from Andrarum. I am convinced that the method of analysing suspended matter can be useful both in environmental monitoring and in mineral exploration.

There is a close connection between environmental geology and mineral exploration (Fortescue 1980). Such a connection is seldom obvious because those working in these different fields of study are often antagonists.

## 5.3 DRAINAGE WATER FROM THE OLD ALUM INDUSTRY

### 5.3.1 Sampling stations in the mining area

A preliminary study of pH and electrical conductance of water in Andrarum showed that several different types of water occur (Carserud 1978a). The positions of the sampling stations were chosen in accordance with this investigation.

Natural springs occur in the gravel overburden. Two have been sampled, one is used in the following account "Södra Brottet". Joints in the shale carry water, which is discharged at several places. Observation wells in shale debris at the foot of the former working front were dug at two places with a hand auger, one is registered here, "Djupet".

Two wells were dug in the waste piles. In one, "Åfyren", only rather consolidated burnt shale was encountered. In the second, "Nya Fyren", gravel mixed with raw shale was found below 1.5 m of burnt shale.

The course of the drainage was changed about fifty years ago. I estimate that 90% of the effluent is drained by the modern concrete culvert. This sampling site is called "Nya Avloppet". The old drainage, "Gamla diket", carries very little water. Its composition of probably influenced by the wastes in and around the old boiler house.

The river water has been sampled about a kilometer upstream the alum industry at "Forsemölla".

The ground water probably carries divalent iron. However, it is quite conceivable that the observation wells will aid diffusion of oxygen to the ground water. Precipitation of ferric hydroxide would greatly influence the chemistry of

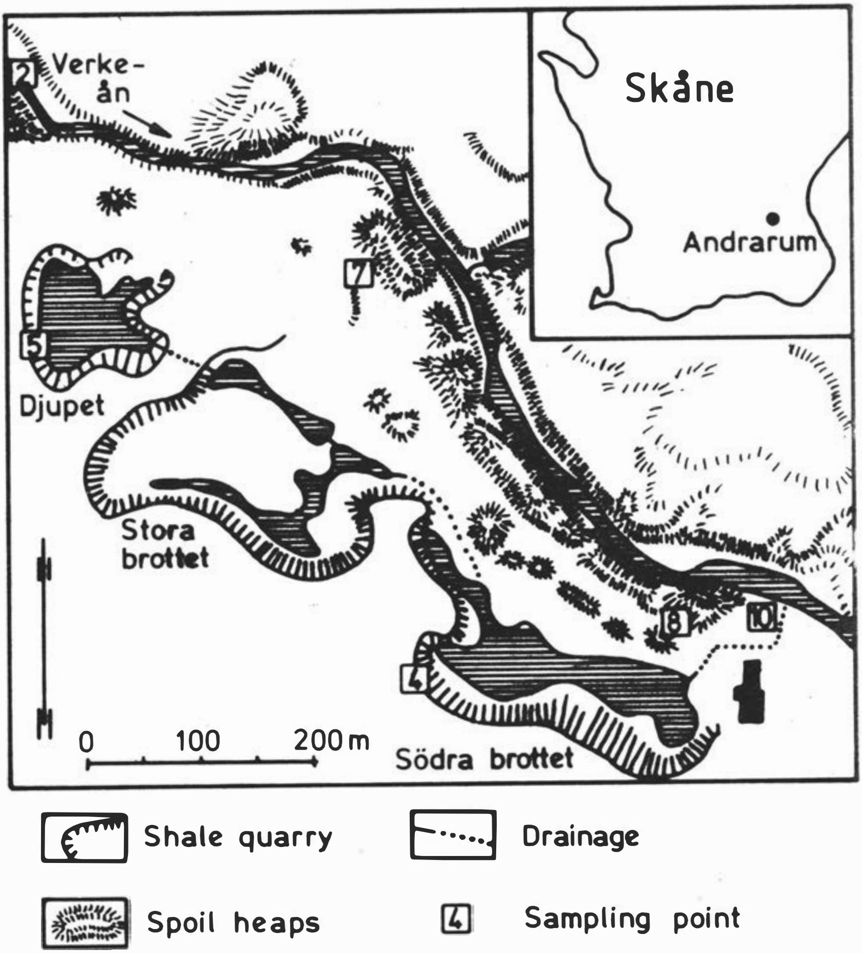


Fig. 2. Map of the alum works at Andrarum

the water in the observation wells. I have not been able to counteract or compensate such effects.

The positions of the sampling stations are shown in Fig. 2. My interpretation of the stratigraphy is shown in Fig 3. The hydrochemical analyses are given in Table 1.

### 5.3.2 Analytical methods

Two bottles of 0.5 l were taken at each sampling point. 5 ml of ultrapure concentrated nitric acid was added to the first bottle. Within 24 hours pH and bicarbonate was determined on the second bottle. Both bottles were filtered through a 0.45 µm membrane filter. The first bottle was kept frozen for later trace metal analysis while the second was kept in a refrigerator for major element analysis.

The measurement of pH was made electrometrically. Bicarbonate was determined by direct titration, sulphate by turbidimetric methods and chloride by indirect titration. The major elements, Ca, Mg, Na and K together with the minor elements Al, Fe and Mn were analysed by atomic absorption spectroscopy.

The trace elements Cu, Zn, Pb, Ni and Ti were detected and analysed by Proton Induced X-ray Emission, PIXE. A complex-forming component was added to the water and the metal complexes were adsorbed on activated carbon. This was then collected on a filter and formed into a pellet, which was analysed by PIXE (Akselsson & Johansson 1979). The analysis was performed by Eva-Märta Johansson, Department of Nuclear Physics, Lund.

The analysis of water is no easy task. Even qualified laboratories can produce analytical results with large errors (Ellis 1976). The result of a major element analysis can be checked in several ways (APHA 1965). For instance, there should be as many negative charges as there are positive. This is checked when the analysis is calculated as equivalents per liter. A difference of 5 per cent is generally considered acceptable. However, some of my analyses showed a 10 % and even a 15 % deviation.

The sum of the calculated ionic conductances should be close to the maximum conductance of the sample. This conductance is measured on diluted samples, to compensate for decreasing ionic activity at high concentration. These values also coincided within a margin of 10-15 %.

Trace elements are even more difficult to analyse correctly than the major elements. Contamination is a serious problem. Some elements also tend to be adsorbed on the wall of the container. Water samples can also age and change their composition upon storage.

I have not done any systematic study of these errors. However, dual analyses of some elements have shown that the data usually differ by a factor of two, without any trend.

The analytical difficulties show that the chemical data of the water samples have to be interpreted with caution. However, I consider them to be good enough for my preliminary conclusions.

### 5.3.3 Types of water

Analyses of the water samples are given in Table 1 and shown in Fig. 3. Glacial deposits of sand and gravel cover the bedrock of alum shale. The water in this material is neutral with a large buffering capacity due to bicarbonate ions and it has less than 400 mg/l of dissolved substances.

Water emanating from the alum shale has a low pH and a lack of bicarbonate. The amount of dissolved substances is generally comparable to that in spring water from the glacial deposits.

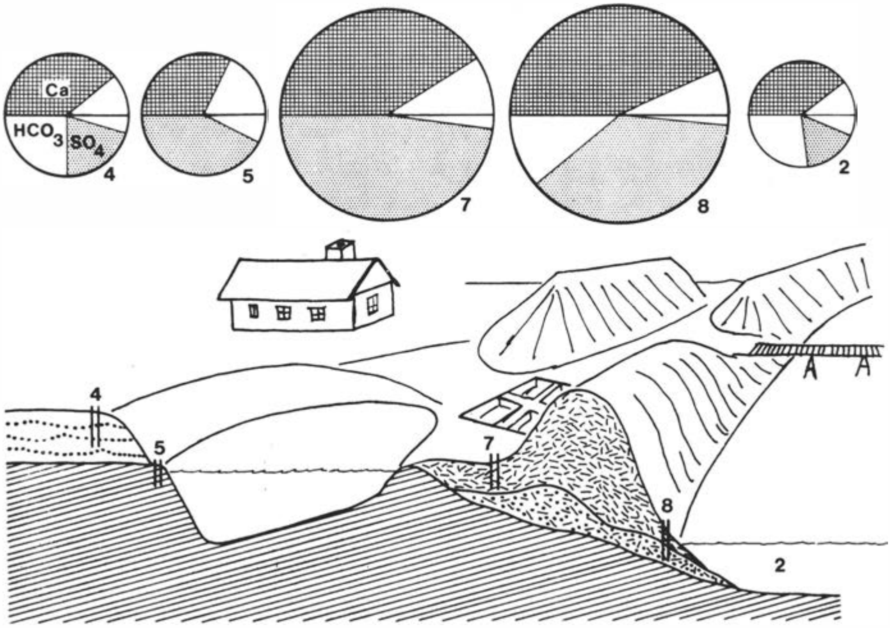


Fig. 3. Ideal cross-section of the alum works at Andrarum. The composition of the water is shown in circular diagrams. The numbers refer to the sampling stations, see Fig. 2 and Table 1.

The burnt shale gives the water a low pH and more than doubles the amount of dissolved substances. Where gravel is mixed with the shale spoils the acidity is neutralized, presumably due to grains of calcite in the gravel.

The acidity is also neutralized when acid water is mixed with water from the natural springs in the gravel. The effluents from the area are therfore neutral, although it has as many dissolved substances as the groundwater in the spoils.

| Water type | River | Spring | Shale | Spoil | Spoil | Effluent | River | Spoil |
|---|---|---|---|---|---|---|---|---|
| Location | Forsemölla | Södra brottet | Djupet | Åfyren | Nya fyren | Nya avloppet | The Earth | Ranstad |
| Sampling point | 2 | 4 | 5 | 7 | 8 | 10 | | |
| Conductance µs/cm | 330 | 420 | 420 | 1000 | 1200 | 885 | - | - |
| pH | 7.4 | 7.8 | 3.4 | 4.0 | 6.9 | 7.3 | - | - |
| Ca mg/l | 63 | 95 | 44 | 238 | 263 | 204 | 15 | 570 |
| Mg " | 2.7 | 2.4 | 3.1 | 6.6 | 5.4 | 7.7 | 4.1 | 80 |
| Na " | 8.6 | 9.8 | 12.2 | 12.9 | 7.6 | 6.7 | 6.3 | 16 |
| K " | 3.7 | 1.9 | 3.2 | 26.3 | 9.9 | 4.5 | 2.3 | 120 |
| $HCO_3^-$ " | 155 | 212 | 0 | 0 | 208 | 106 | 58 | |
| $SO_4^{--}$ " | 49 | 45 | 112 | 650 | 550 | 500 | 11 | 2100 |
| $Cl^-$ " | 15 | 19 | 15 | 15 | 14 | 14 | 8 | - |
| Fe µg/l | 300 | 7800 | 1100 | 10800 | 300 | <100 | | 1200 |
| Mn " | 100 | 200 | 800 | 500 | 200 | <100 | 7 | 10000 |
| Cu " | 6 | 30 | 30 | 20 | 20 | <5 | 7 | 100 |
| Zn | 10 | 80 | 50 | 140 | 110 | <5 | 20 | 500 |
| Pb | 2 | 30 | 70 | 20 | 80 | <5 | 3 | - |
| Ni | 6 | 20 | 10 | 20 | 30 | <5 | 0.3 | 300 |

Table 1. Chemical composition of water from Andrarum, compared with other types of water. See Fig. 2 for sampling points. Fig. 3 shows the major element composition in circular diagrams.

## 5.4 GEOCHEMICAL BARRIERS

There is a contradiction between the high content of heavy metals in the water inside the industrial area at Andrarum and the low content in the water leaving this area. Obviously a process of self-purification takes place. The purification is best explained by geochemical barriers. Such a barrier has been described as a boundary, where conditions of migration change drastically (Perelman 1977).

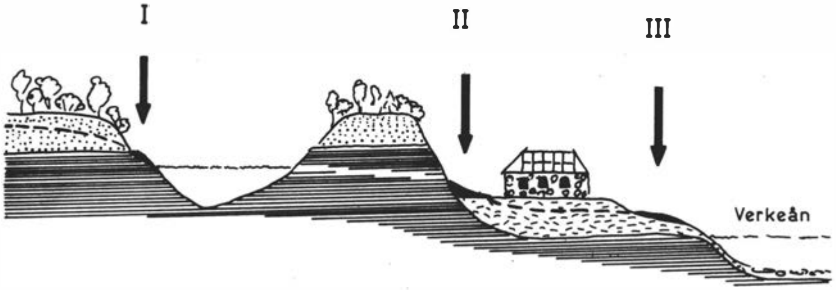
The geochemical barriers are commonly caused by physical or chemical factors like pressure, temperature, pH or Eh. A drop in the migrational ability at the barrier results in concentrations of chemical elements (Perelman 1977, Fortescue 1980).

In Andrarum there are two different types of barriers: neutralizing and oxidizing. Despite the unplanned deposition of the shale residues, the results have been quite advantageous.

The over-burden of sand and gravel contains a fair amount of limestone. Shale residues were put on top of the redeposited over-burden, which neutralizes the acid water emanating from the leaching of the shale, see Fig. 3.

Many heavy metals are dissolved in acid water but precipitated in neutral. The sequence of the over-burden below, and weathering shales above, therefore, is a neutralizing barrier.

Only a minor part of the precipitation flows through the heaps of shale residues into the river. Most of the water follows the old drainage channels, which were built to keep the mining area dry.



| I | | II | III |
|---|---|---|---|
| Gravel | | Shale | Spoil |
| 1x | Cobalt | 5x | 50x |
| 1x | Copper | 25x | 20x |
| 1x | Lead | 3x | 20x |
| 1x | Nickel | 4x | 35x |
| 1x | Uranium | 2x | 5x |
| 1x | Zinc | 2x | 7x |

Figure 4. Ideal length-cut through the alum works at Andrarum. Water from gravel, shale and spoils deposit iron precipitates. The table shows the relative concentration of heavy metals in these. The concentrations in deposits in water from gravel are used as unit values.

Over a distance of some 700 meters the surface of the water drops 8 meters. At some places the water flows through underground tunnels and at other places it flows in the open air. Large amounts of yellow-brown precipitates of ferric hydroxide can be seen along the internal water-courses. The precipitate is commonly called "yellowboy" in colloquial American-English.

The samples of ferric hydroxide have been analysed. The analysis was made with JUMBO, an apparatus for atomic emission spectroscopy formerly used at the Swedish Geological Survey. One sample, from "Gamla Diket" was also analysed with PIXE. The results of the dual analyses showed large deviations. The concentrations of elements in ppm in dried material was for JUMBO and PIXE respectively: Ni 1100-150, Cu 830-280, Zn 770-390, Pb 710-530 and U 400-220.

These contradicting results cast a shadow on the accuracy of the analyses. However, I have assumed that all three JUMBO-analyses suffer the same analytical errors and therefore I have normalized the data to the analysis of the natural spring, see Fig. 4.

Precipitates from water coming from the weathering of the alum shale contain higher amounts of all heavy metals. Yellowboy from the old ditch, which mainly drains the ground on which the old boiler house stands, has conspicuously high concentrations of heavy metals.

Iron is precipitated when it is oxidized from the ferrous to the ferric state.The oxidation state is thus a chemical barrier to iron. Some other elements behave in the same manner, for instance manganese. Many of the heavy metals, however, are adsorbed onto the ferric precipitate, which acts as a scavenger. This could be called an adsorbing geochemical barrier. Presumably this is the major process responsible for the self-purification of water from heavy metals.

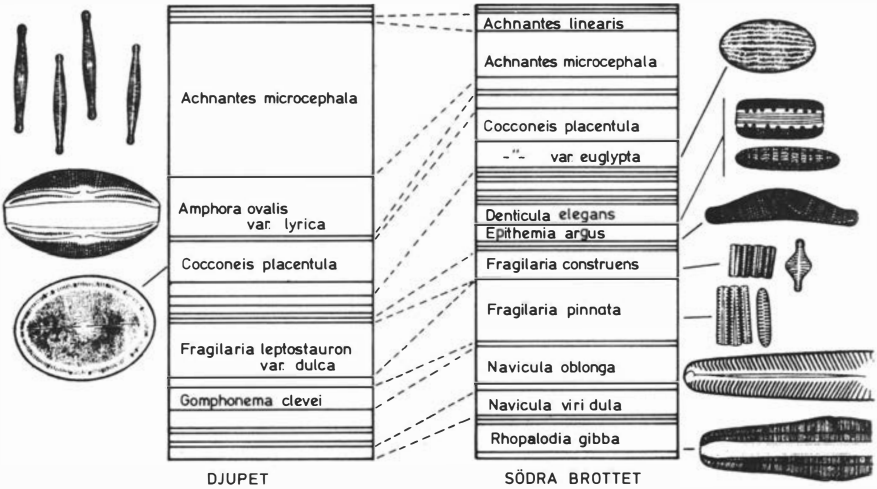


Fig. 5. Concentration of diatoms in sediments from the lakes "Djupet" and "Södra Brottet". The analysis of diatoms has been performed by Mrs. Hanne-Lore Håkansson, Dept. of Quaternary Geology, University of Lund.

## 5.5. LOCAL ECOLOGICAL EFFECTS

The effluent water, leaving the old alum factory, has but little dissolved heavy metals though the concentrations of calcium, potassium and sulphate are quite high. These substances are not poisonous but they affect aquatic plants and animals.

Within the shale mining area there are two small lakes. One of them, "Djupet", is mainly supplied with water from springs in the gravel above the alum shale, and is therefore hardly influenced by chemical weathering of the shales. The concentration of dissolved substances is about 350 mg/l.

The other lake, "Södra Brottet", receives water both from unpolluted springs and from weathering shale and shale residues. The water has about 850 mg/l of dissolved substances, of which more than half is sulphate.

Diatoms can be used as indicators of the environmental conditions in water. Bottom sediments from the two lakes were collected and studied. The composition of diatoms in the sediments is shown in Figure 5, on the previous page.

The diatoms in the unpolluted lake Djupet are rather common in most lakes in this part of Sweden. However, the polluted lake Södra Brottet had diatoms, which otherwise occur in brackish or salt water.

## 5.6 COMPARISONS OF ENVIRONMENTAL POLLUTION

### 5.6.1. Drainage water compared with the receiving waters

The chemical composition of a polluting discharge can be compared with the composition of the receiving water. A large difference between the two indicates a risk of environmental pollution.

The river water is represented by the sample from "Forsemölla" in Table 1. The effluent is represented by "Nya Avloppet". A comparison shows that the effluent has 2-3 times higher concentrations of all major elements. Sulphate is approximately 10 times higher in the outlet than in the river, see also Fig. 3.

The ground water has high concentrations of several heavy metals. The effluent, however, has concentrations below the detection limit for most metals. This is probably a result of the geochemical barriers mentioned in section 5.4.

The effluent is diluted about 100 times in the river. Consequently the river will not be influenced very much. However, this kind of reasoning can not be applied to a river already polluted, because a large number of small sources of pollution can have profound effects on a river.

The quality of the river itself, therefore, has to be compared with some standard; here I have chosen the average composition of river waters on Earth (Turekian 1969). The river Verkeån has concentrations of the major elements approximately 2-3 times higher than the world average. Trace metal concentrations seem to be of the same magnitude.

From these data no definite conclusion can be drawn. The concentrations of phosphate and nitrate are probably of major importance for the quality of the river. As mentioned earlier the river Verkeån is one of the cleanest in this part of Sweden. My conclusion is thus that the effluent does not considerably deteriorate the quality of the water, although it is sensitive to changes because it is initially so clean.

### 5.6.2 Weathering of black shale in other areas

The analytical data from Andrarum can be compared with data from the weathering of black shales in other areas.

At Kvarntorp, Närke, between Stockholm and Göteborg, black shale has been used for the production of oil. The industry was started during the second world war and ended in 1966. Approximately 50 million tons of shale were processed. The one large spoil heap is a great environmental problem. Several polluting chemical industries have been localized to this already afflicted area. It is difficult to study in detail the effects of weathering and leaching of the shale as there are several different sources of pollution. The water from Kvarntorp has approximately the same composition as water from Ranstad, see Table 1 (Carserud 1978).

Uranium can be extracted from alum shale by using strong acids. Several plans for large-scale mining of the shale have been presented. In one plan called "Ranstad -75" 6 million tons a year of shale were to be processed. This plan was merely a scaling-up of processed already tested on a pilot-scale. The composition of the water passing through the shale has been calculated (SGU 1977), see Table 1.

The maximum concentration of pollutants in Andrarum occur in water in the spoil at Åfyren. The calculated composition of water in the spoil at Ranstad is two or even three times higher. Only iron seems to occur in higher concentrations at Andrarum.

In Estonia, USSR, there are paleozoic black shales, comparable to the alum shale. Weathering of these shales has been studied by Althausen and co-workers (1980). In a brook and a lake, close to the open pit, concentrations of the same magnitude as the maximum in ground-water from Andrarum were observed.

Direct leaching by rainwater of new raw and newly burnt shale gave very much higher concentrations of dissolved substances. The heavy metals Mo, V and U were analyzed. Uranium could occur in concentration above 1000 µg/l in the Estonian waters. This is about twice as much uranium as in water from Ranstad (SGU 1977) and 20 000 times more than in average river water (Turekian 1969).

The authors conclude that there is a serious risk of environmental pollution in the shale-mining areas in Estonia. However, no information is given about the total area affected.

### 5.6.3. Acid mine drainage

Weathering of pyritic material produces ferrous and ferric iron, sulphate and sulphuric acid. Such weathering occur in nature, but the speed and extent is greatly accelerated by mining, where it gives rise to acid mine drainage (Carserud 1978).
In Sweden there are approximately 200 abandoned sulphidic mineral mines. The effluents from these mines are generally acid with about 1000 mg/l of sulphate, 1-100 mg/l of iron and 100-500 mg/l of zinc. Copper is usually less than 10 mg/l and lead about 1 mg/l (Qvarfort 1979). Compared to these figures it it is evident that the effluent from Andrarum is a minor environmental risk.

About 20% of the abandoned Swedish mines are serious sources of pollution of the environment. Other nations have much larger problems with acid mine drainage. In USA there are approximately 88 000 abandoned underground mines (EPA 1975).

The environmental problems are particularly serious in hilly areas with porous sedimentary rocks, where mining lowers the ground-water level. This greatly enhance pyrite oxidation in rocks formerly submerged.

# 6. ENVIRONMENTAL POLLUTION IN THE PAST

The discharge from the alum industry today has very little influence on the river Verkeån. This need not always have been so. The alum production in Andrarum reached its climax already during the first half of the 18th century and was discontinued in 1912. Pollution must have been much more serious during the peak of activity and Verkeån is probably an example of an ecosystem that has recovered from environmental stress.

## 6.1. ATMOSPHERIC EMISSIONS

### 6.1.1 Sulphur dioxide

During the operation of the alum industry sulphur dioxide was released when the shale was burnt. Already at the end of the 17th century the peasants in the surrounding area complained that their crops were harmed by the smoke. Their village was later bought by the industry and no more official complaints were forthcoming (Ture Nilsson, Sillaröd, Lövestad, pers. comm. 1980).

Many visitors have given evidence of the heavy smoke around the factory. The absence of the plague in Andrarum was attributed to the purifying action of the smoke (Andersson 1974).

In 1978 the alum industry was revived for a week. Five tons of shale were burnt according to the old methods. During this week I measured the quality of the air with two different methods: "the lead peroxide cylinder method and "the hydrogen peroxide method" (Carserud 1980). The air around

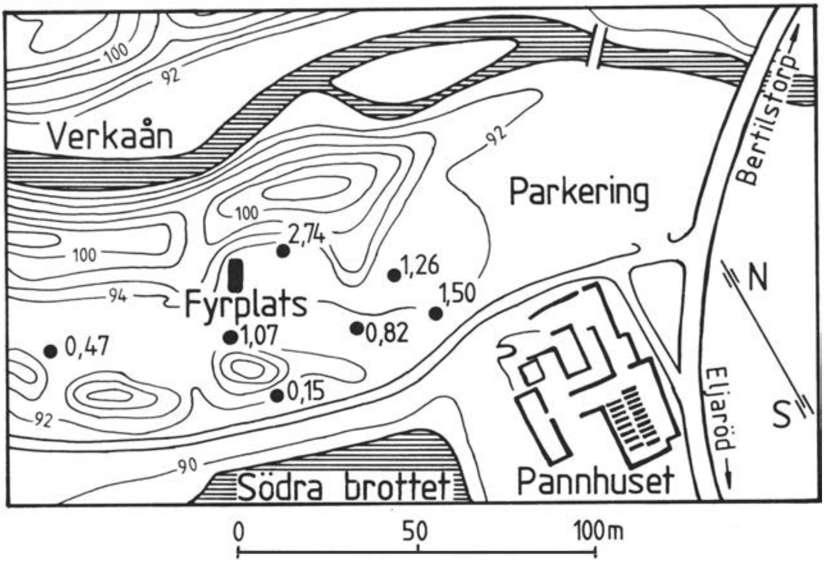


Fig. 6. Concentration of $SO_2$ in the atmosphere around the heap of burning shale (Fyrplats) in 1978. The numbers in bold type give the concentration measured by the lead peroxide cylinder method. The other numbers show the topography.

the heap of burning shale contained about 100 µg $SO_2$ per $m^3$ of air, that is about the same quality as dirty city air.

It is not possible to calculate the total emitted $SO_2$ from an analysis of the air, as topography, wind speed and wind direction influence the result. This is clearly shown in Fig. 6, where the data from the lead peroxide cylinder method are presented.

When the alum industry was in operation, approximately 10 000 - 20 000 tons of shale were burnt every year, most of it during the summer, that is, several hundred times more than was burnt in 1978. Thus it is quite evident that the smoke must have been thick around the alum works.

Sulphur dioxide is only slightly soluble in water. It is oxidized to sulphur trioxide in the atmosphere. As the $SO_3$ is easily soluble it is washed out of the air by rain. The half-life of the oxidation is a couple of days and therefore the sulphur from the industry was deposited over a large area, several thousands of $km^2$.

However, $SO_2$ can also become adsorbed onto soot and other particles. A substantial amount of $SO_2$ was therefore deposited in the surroundings of the factory.

The total emission of sulphur dioxide during the test-burning in 1978 was estimated by analyses of raw and burnt shale. Eight samples showed an average concentration of 4.0 % S prior to burning and 5 samples of burnt shale had an average concentration of 1.8 %. This would indicate that more than 50 % of the sulphur went into the air.

This is probably a maximum value. due to inefficiences in the test-burning. On large-scale burning the heaps were 100 times larger. Large, slowly burning heaps facilitated chemical reactions between the $SO_2$ produced and the minerals present.

In Andrarum 82 500 tons of alum and some 30 000 tons of vitriol were produced from 738 200 $m^3$ of shale (Stoltz 1932). This corresponds to an extraction of about 8 g of sulphur per kg of shale.

I leached the shale from the test-burning four times in the laboratory. About 5 g of sulphur per kg shale could be extracted. This shows that the efficiency of the test-burning was lower than that of the industry. This would also indicate that more $SO_2$ could be retained by the large spoil heaps and that not more than 30-35 % of the total sulphur in the shale was emitted to the atmosphere as $SO_2$-gas during the activity of the industry.

The average concentration of sulphur in the shale is 6 % (Westergårdh 1944). At peak intensity some 20 000 tons of shale were burnt every year and consequently a maximum of some 700 tons a year of $SO_2$ was emitted from the alum industry.

In comparison to modern standards, this is a small amount. For instance, the central heating of a Swedish town of 40 000 inhabitants demands combustion of some 75 000 tons of oil a year with a concomitant emission of 1400 tons of $SO_2$ (Carserud 1980).

The total emission of $SO_2$ nowadays, however, is clearly a threat to nature, as witnessed by the increasing numbers of acidified lakes in Sweden. The acid rain caused by present-day combustion of fossil fuels surpasses in only a few years the regional effect of $SO_2$ from the alum industry during 275 years of activity. Therefore it is not possible to trace any regional acidification caused by the alum industry. However, the $SO_2$ from Andrarum was not let out through high chimneys but at ground level. The local influence might therefore have been considerable.

### 6.1.2 Emission of selenium and zinc

I expected the smoke to contain other elements than sulphur. During the revived shale-burning in 1978 I observed yellow crystals forming on top of the burning shale heap. I let the smoke pass under a cold surface, onto which small greyish crystals soon condensed. The crystals were scraped off and later analysed witht PIXE.

The analysis showed that the deposit consisted mainly of sulphur but it contained also 2.3 % Cl, 630 ppm F, 710 ppm Br and 310 ppm Se. Obviously the halogens Cl, F and Br were driven off from the shale during the heating.

Selenium is an element with a high vapour pressure. Other elements with high vapour pressures are As and Zn, which were found in a few ppm. Neither cadmium nor mercury were found.

Selenium occurs in most samples of the shale at a concentration of about 4 ppm. Burnt shale has been analysed and Se has no been found above the detection limit, which is 3 ppm (Carserud 1982b). Conclusions are therfore uncertain, but it can be safely assumed that between 10 to 80 kg of Se a year were released form the alum industry during it heyday.

Today,about 7 tons of Se a year are emitted into the atmosphere in Sweden, mainly from combustion of fossil fuels (Laveskog et al. 1976). In relation to this amount the emission of Se from Andrarum was quite considerable, at a single site.

The hydrogen peroxide method of monitoring $SO_2$ in air uses a constant flow of air which is bubbled through an impinger containing a dilute solution of hydrogen peroxide. This solution is then analysed for $SO_2$. I used the same solution for an analysis of zinc by atomic absorption spectroscopy with a carbon rod atomizer. The analytical data showed some irregularities. The solution was kept in plastic bottles for a long time before analysis. Plastic usually contains some zinc, which can contaminate the samples. In addition, I have no information as to whether all zinc in the air sample would be trapped in the hydrogen peroxide or not.

Due to these uncertainties in the analysis, the average concentration of zinc in the air can only be given as a very rough figure, around 1 µg/m$^3$. This can be compared with the concentration of zinc in the atmosphere in urban areas in USA, which is 0.01 - 0.84 µg/m$^3$ (Laveskog et al. 1976).

The concentrations of $SO_2$ and zinc,in the air around the burning shale pile, seem to be comparable to a very dirty urban atmosphere.

## 6.2 EFFLUENTS FROM THE INDUSTRY

The alum manufacturing process has been described for many different industries and seems to be essentially the same in most places (Geschwind 1901, Singer 1948, Andersson 1974), see also Fig. 1.

The leachate from the burnt shale was concentrated by boiling and then left to crystallize. The remaining "mother liquor" was used again to produce vitriol or more alum. During the evaporation,precipitates of iron were deposited as incrustations in the concentrating vessel or as a mud in the cooling tank. The iron precipitate was saved for later manufacture of red ochre.

Large amounts of wood and peat were used for the evaporation. The ashes were washed to extract pot-ash, which could be sold or used in the manufacture of alum.

From this short description of the processes it is obvious that the industry produced very little effluents. The actual water pollution was therefore insignificant.

## 6.3 WEATHERING OF THE SPOIL HEAPS

### 6.3.1 Chemical analysis of weathered processed shale

Some minerals are more susceptible to weathering and leaching than others. In soil science a comparison of the chemical analysis of samples from different horizons is often used to show the degree of weathering in a soil.

The intensity of weathering in the spoil heaps of burnt shale can not be studied in this way. There is a slight change in the composition of the shale and the expected differences due to weathering are small. However, I have assumed that material within a volume as small as a couple of litres has the same original composition.

Three such samples from the spoil heaps have been separated into a coarse and a fine fraction. Due to its larger surface area the fine fraction ought to be more thoroughly weathered than the coarse fraction. The samples have been analysed by conventional methods for the major elements. The same samples have also been analysed with PIXE, which have given data for 27 elements.

In studies of weathering it is common to standardize the chemical analysis with respect to some unaffected element, usually aluminium (Birkeland 1974). The differences in the major element composition in the different fractions of shale spoils is small. Therefore comparisons have been made without standardization.

One of the most soluble elements in an oxidizing environment is sulphur. The sulphides are oxidized to sulphate, which is very soluble and is therefore carried away with the percolating water. The effects of weathering therefore would be most notable for sulphur.

The three different samples had a 6, 13 and 49 % lower sulphate content in the fine fraction than in the coarse. However, the analyses have some important errors. The undeterminate analytical error in the sulphur determination is only 1 %. But an error of approximately 8 % is introduced because the sample size analysed by PIXE is very small (Carserud 1982b). These errors in two compared samples would, according to the laws of statistics, amount to 11 %.

In order to have a 95 % significance for evidence of weathering, the difference between the samples should be more than 11 %. The same statistical calculation can be made for the other elements.

Some elements show evidence of intensive leaching, namely Se and Br. Other elements seem to remain fairly unaffected, viz. V, Ga and Y. The remaining 14 heavy metals show peculiarly contradicting results. In one sample these elements, together with sulphur, are strongly depleted in the fine fraction, but in the two other samples they are enriched in the fine fraction.

There are several possible explanations for these results. In any case it is not possible to draw any conclusion concerning the degree of removal of these elements in the industrial process and the subsequent weathering.

### 6.3.2 Calculation of leaching rates

#### *6.3.2.1. Laboratory leaching*

Three samples of spoil from Andrarum have been leached in the laboratory (Carserud 1981). I used the material I got when I dug the observation wells "Djupet", "Åfyren" and "Nya Fyren".

The samples were leached with hot water in Soxhlet extractors. The laboratory leaching showed that lack of oxygen was the limiting factor for sulphide oxidation in the spoil heaps.

Oxygen has to diffuse from the soil surface, through moist soil, through a surface film of water around the mineral grains and eventually through a part of the rock. The rates of diffusion in different media is known only within wide limits. However, it is probably the two last steps that limit the overall diffusion rate.

An element in a rock occurs in positions which are more or less susceptible to leaching. It depends on the type and size of mineral in which it occurs, the permeability of the rock and the total rock surface.

Experience from the laboratory leaching shows that the rate of leaching can be described as an exponential function of the form:

$$C = C_o \cdot \exp - k \cdot t$$

$C_o$ and $C$ is the initial and present quantity of an element brought away yearly by water percolating through the spoil heaps. This equation can be integrated to yield:

$$A = \frac{C_o}{k} (1 - \exp - k \cdot t)$$

"A" in this equation is the total amount of an element leached away during the time "t".

### *6.3.2.2. Estimation of the total amount of sulphur leached*

The amount of sulphur leached can be estimated. The alum shale contains an average of 6 % sulphur (Westergårdh 1944). Nine samples of burnt shale residues have been analysed giving an average concentration of sulphur of 2.1 %.

The amount of sulphur emitted during the burning has previously been estimated to 30 % of the sulphur, that is 1.8 %. The amount of sulphur in the products corresponds to an extraction of 0.8 % (see sect. 6.1.1). There now remains 1.3 % of S per kg shale unaccounted for. This is the amount that must have been removed by weathering since the time of the deposition.

The total amount of shale mined was some 2 million tons. Some was dumped in the river and some was deposited below the groundwater level. A very rough estimate is that about 1 million tons of shale have been weathered and about 13 000 tons of sulphur, which is equivalent to 39 000 tons of sulphate, have been leached away.

The period of leaching is not the same for all spoil heaps as the industry was active for 275 years. The peak of production occurred during the second half of the 18th century. A leaching time of 200 years can thus be used as an average figure.

The drainage water comes from an area of about 0.5 $km^2$. About a third of the annual precipitation of 600 mm is infiltrated. The average runoff is thus 100 million litres per year. The present concentration of sulphate in the effluent is 500 mg/l (see Table 3). Consequently 50 tons a year of sulphate is nowadays leached from the spoil heaps.

### *6.3.2.3 Calculated initial leaching of sulphur*

The two equations from the previous section can now be solved: C = 50 ton/year, t = 200 years, A = 39 000 tons. The result of the calculation shows that the initial quantity of sulphate leached away, $C_o$, was around 500 ton/year. This is equivalent to a sulphate concentration in the drainage water of 5000 mg/l, ten times its present value.

The common range of sulphate concentration in acid mine drainage is 500 - 20 000 mg/l (EPA 1975). The effluents from Andrarum are evidently within this range.

The river Verkeån has about 50 mg/l of sulphate and its volume is about 100 times larger than the drainage from the alum industry.

The addition of effluents with a concentration of 5000 mg/l of sulphate would double the amount of sulphate in the river. However, sulphate is not a toxic substance. Far more important is the addition of acidity. If all sulphate were present as sulphuric acid the effluent would contain a maximum of about 100 milliequivalents per liter of acid.

The river water has a buffering capacity of approximately 5 mekv/l. As the volumes of water in Verkeån are 100 times larger then the effluents this would be more than enough to neutralize the acidity.

The initial concentrations of other elements in the effluents can be calculated in the same manner. However, the primary data do not show alarmingly high concentrations and they are too uncertain to merit further calculations.

My conclusion from the calculations above is the the outlet of drainage waters from the spoil heaps at Andrarum did not seriously change the chemistry of the river Verkeån.

## 6.4. DUMPING IN THE RIVER

During the 275 years of industrial activity 505 340 $m^3$ overburden consisting of sand and gravel and 1 243 540 $m^3$ shale were excavated (Stoltz, 1932). In many modern mines this amount is excavated annually. Thus is was a comparatively small undertaking, but all the material was dug up with pick-axe and shovel and transported by wheel-barrows.

It was of vital importance to keep transportion distances to a minimum. The area available for dumping was small and therefore the river was used. First, only overburden was dumped, but later also burnt shale.

Dumping in the river was particularly common at the end of the 17th century. At that time several different investors tried to get as much money as possible out of the industry.

The river was choked and serious flooding occurred downstream. The river bed had to be deepened at great cost. The authorities tried to prevent river dumping by imposing fines, obviously without much success.

Later the spoils were wheeled on a bridge across the river and dumped on unused ground on the other side. However, the river itself continued to erode into the steep banks of wastes. The river bed is now finally fairly stable with an exotic bottom surface of baryte concretions remaining from the washed spoils.

About half of the burnt shale was taken away by the river. Much of it has been transported to the sea, but most of it has been deposited on low-lying parts of the river valley. Approximately 2 $km^2$ of the valley floor downstream of the alum works is covered with burnt shale to a depth of 0.2 - 0.3 m.

### 6.4.1 Effects on the river

The river flows through a region with large deposits of glaciofluvial material. The dumping of gravel and sand therefore could but augment an already occurring transport of naturally eroded material.

In contrast, the burnt shale is different, both chemically and physically. During the transport the shale fragments are broken, disaggregated and dispersed to clay. The environmental effects of the dumping is caused by changes in the chemistry of the river and increased turbidity and siltation. Fishing and farming were affected.

The alum factory belonged to Christinehof Castle. The history of hunting and fishing on this estate has been studied by Rolf Edling. He found no documents indicating a decrease of fish in the river due to environmental pollution (Rolf Edling, Lund, written comm. 1979). However, this could be due merely to a lack of documentation.

The conditions in the river Verkeån could be compared to an incident in the river Thames at the beginning of the 17th century. The war with France (1626-28) made the North Sea dangerous. English alum factories in the Tees district had problems in getting coal and shipping alum. Therefore they brought the shale to London. Not far from the Tower the shale was burnt and leached. The refuse was thrown into the Thames. The inhabitants then complained of a detestable stench, fish died, cattle refused to feed on the pastures, prevalent sickness was ascribed to the new works. Alum-making in London was discontinued when the war ended in 1628 (Singer 1948).

Written complaints about the conditions in the Verkeå river are not to be expected. Already quite early a harbour was planned at the mouth of the Verkeå river. Large tracts of land along the river were bought by the first owner of the shale factory. Conflicts of interest would then not concern the public.

Other types of evidence can be used to estimate the effects of environmental pollution on the river Verkeån. At the mouth of the river there is a stationary fish trapping tackle called "Öradekaren". This has been in use almost without interruption for three centuries. Obviously the fishing must have been profitable, which contradicts any evidence of serious pollution.

At the alum factory the river has a drainage basin of 50 $km^2$. The average runoff is 11 l per second per $km^2$ (Tryselius 1971). The amount of waste from the alum factory transported by the river during 275 years of activity is approximately 1.5 million tons. From this it can be calculated that the average concentration of suspended matter in the river was approximately 400 mg/l. The peak concentration must have been much higher.

The present average concentration of suspended matter in the river is less than 10 mg/l (Carserud 1982a). The transport of sediment at that time was 40 times greater than its present value.

Swedish rivers have an average load of approximately 10 mg/l or less. However, rivers in other regions have much higher suspended load. For instance, the average concentration of suspended matter in American rivers is 602 mg/l (Judson & Ritter 1964).

Evidently the great increase in sediment transport must have greatly influenced the ecology of the river. However, several circumstances have limited the damage to the fishing. The increased turbidity of the water was detrimental but not mortal to the fish. They were able to swim through the polluted parts of the river to spawn in the undisturbed tributaries.

About two thirds of the suspended matter has been deposited in the river basin. Parts of the valley floor functioned as a sediment trap. After passing these areas the river water was considerably less turbid than before.

The largest suspended load is carried at high water. It is quite probable that most of the sediments were eroded and deposited on occasions of extreme run-off, which do not occur every year. Consequently the water would have been cleaner in the intervening periods.

The worst polluted parts of the river must have been a barrier for the movement of fish. However, halfway between the factory and the largest sedimentation basin there are waterfalls, Hallamölla, which trout and other fishes can not pass. The polluted reach of the river then did not significantly change the spawning habits of the salmon, because a barrier was already present.

### 6.4.2 Effects on farming

The fine-grained debris deposited by the river is locally called red-earth (sw. "rödjord"). Formerly the meadows along the rivers were used mainly for grazing or hay-making. Large-scale deposition of red-earth could be expected to have deleterious effects. However, from a farmer I heard that the red-earth was quite productive.

In order to test this I took four samples of recent river sediments and three samples of red-earth. The samples were analysed for easily soluble phosphate and kalium, together with nitrate, magnesia, calcium and boron. The analysis was done at an agrochemical station with methods standardized for investigation of arable land. The analyses showed that recent sediments are more rich than the red-earth in all nutrients but potassium.

However, the valley floor is not covered everywhere with recent sediments. Large parts is covered with late-glacial sand and silt resulting from the erosion of glacial deposits by melt-water from the wasting ice.

This late-glacial sand is probably far less nutritius than the red-earth. The latter also has a much better capacity to retain water and thus sustain vegetation during dry summers. Therefore the sedimentation of red-earth actually could be an advantage to the farmers.

## 7 ENVIRONMENTAL POLLUTION IN THE FUTURE

The leaching of sulphur and heavy metals will continue for many hundreds of years, only slowly decreasing from the present value, which does not pollute the environment to an appreciable degree.

The heavy metals in the geochemical barriers of precipitated iron might be susceptible to migration. If the deposits of ferric hydroxides is put into an acid and reducing environment the heavy metals could be leached away. This could happen if the ground water level was changed or if the ferric precipitates were covered with soil. However, the alum industry at Andrarum is nowadays a historical site, preserved by law. Therefore no changes are planned.

## 8 CONCLUSIONS

The alum industry at Andrarum has not caused any permanent damage to the ecosystem. The low pollution from leaching and weathering of the shale residues have several reasons. The concentrations of pyrite and other minerals containing heavy metals in the shale are relatively low. The shale has a low permeability and the burnt shale was carefully washed before final deposition. A very interesting feature is the obvious self-cleaning from heavy metals caused by geochemical barriers. This effect might be used for purification of water in other connections.

The most deleterious pollution was probably caused by dumping of over-burden and shale into the river. The river ecosystem must have been seriously stressed by this bad practice. However, the dumped material was not toxic and fishes could survive and spawn in unpolluted tributaries.

The emission of sulphur dioxide was large, but the regional effects are small in comparison to the effects caused by the present pollution of the atmosphere due to combustion of fossil fuels.

In comparison to most modern mining undertakings the alum industry at Andrarum was small and the rate of mining very low. This is of course a major factor in explaining the relatively insignificant environmental impact of the alum industry.

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