Fluoride contamination of water stream in Moscona Mine area, Asturias

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ABSTRACT
The extent to which fluorite mining of Moscona mine influences surface and groundwater quality in the Lavares stream area is evaluated in this paper. Hydrogeochemical analyse of mine water were carried out and have revealed that total dissolved solids, carbonate and sulphate, hardness and fluoride content are high. As a result fluorite mining has caused significant degradation in ground water quality. One special peculiarity of this fluorite field is that the mine water does not have acid mine drainage problem as the mineralized deposits are not associated with pyrites and sulphur content.
Underground mining in Moscona produce a considerable volume of polluted water and each year 200.000 m^3 of water is pumped out of the mine to the Lavares stream. Reduction and control of the contamination measures preserve stream conditions in an acceptable quality level in accomplishing wit Spanish regulations.

INTRODUCTION

Asturias fluorite mines are the repository of more than 90 % of Spanish fluorite reserves. Mining of fluorite are related with Triassic volcano sedimentary deposits in the Centre and East area of Asturias (Iglesias, J.)(1). All the material is removed by underground mines and treated in a concentrator plant sited in Ribadesella.
By far the main use of fluorite or fluorspar is as the source of hydrofluoric acid, which is a feed chemical for a multitude of processes that produce thousands of inorganic and organic fluorine compounds, including insecticides, pharmaceuticals and fabric conditioners.
Mining the mineral leaves solid waste and the extracted waste still has very high concentrations of fluoride. Another consequence of underground fluorite mining is a relative huge volume of polluted water, flooded in the mines. If these effluents are thrown into the streams they in turn get chemically polluted. Activities other than mining like fluorite beneficiation and preparation also generate huge amounts of water effluent which affects the aquatic ecosystem and produce contamination and even health effects on humans and livestock.
Hydro geochemical analysis of mine water was carried out in one of the fluorite mines of Minersa Company. The analysis revealed that the total solids and fluoride content are high. Acid mine drainage problem is not observed, neither biological contamination are observed in the mine water.

STUDY AREA

Moscona fluorite mine is one of the three mines operated by Minersa Company in Asturias. The mine is situated in Llanera council in the central area of Asturias, 25 km north from Oviedo, in a zone around 43º 24’ 28” N latitude and 02º 04’ 08” W longitude. The mine reaches 1 km from East to West, 2 km from North to South and has a medium thickness of 4 meters. The stratification is 10º NE dip. The mine is situated at a depth of 300-400 meters below the ground. In 2004, the production amounted to a total of 140.000 tonnes of fluorite or fluorspar.

GEOLOGY

Geologically, the study area includes two well differenced sets: Palaeozoic materials and Mesozoic deposits that lie discordantly over that. All have been affected by the Alpine deformation, characterized by the existence of big fractures, mainly NW-SE:

- Palaeozoic: Devonic materials are present in this area. Limestone and dolomites take turn with shale in thickness up to 700 meters, in the Rañeces formation, that is at roof. Underlying with it, it is another formation, Moniello, in which limestone inserts with marls and slates. At wall, there is a sandstone formation, Naranco, with a thickness of about 300 m.
- Mesozoic: In the study area there are Triassic and Jurasic deposits. Triassic formation appears discordantly over Palaeozoic basement, from wall to roof, four levels are well differentiated. First a detritic formation, made up of siliceous conglomerates, coarse sandstone and some carbonated bed upside, with 50 meters thickness. Next a calcareous level, of about 15 meters thickness, where mineralization takes place, and over it another stratified detritic formation of 40 meters thickness. Overlying with them a marl level up to 200 meters thickness with red marls, and fine sandstone and gypsum beds alternating wit clay. Over Triassic materials there is a calcareous-dolomite Jurassic sedimentation, corresponding to Liassic period, followed by a potent Dogger conglomerate series.

The fluorite deposit is masive and stratified type, close to fracture zones, NW-SE and E-W faults, the mineralized bed may has more than one kilometer extension, perpendicularly to techtonic structures, with 2,5 to 4 meters medium thickness. Mineralizations are mainly related with Permian or Permotrias sediments, replacing carbonate levels, showing hetereogeneous structures, karstic, breachform, with vertical little veans.

DESCRIPTION OF THE MINE

Located in the central area of Asturias region, the Moscona fluorspar mine is exploited in three different levels, divided by two faults. The mine is an underground room and pillar operation, perforation is made with jumbos and extraction is made with explosives (García, G.) (2)

Fluorspar mineralization locates in the roof of a calcareous formation from Muschelkalk with a total thickness between 3 and 4 meters. The deposit is set dipping 10º NE, close to the Palaeozoic base.

Mineralized bed is made up mainly by fluorite, silica, and calcite and in less proportion, barite, pyrite, coveline, azurite, malaquite and some galena. Mineral from Moscona mine has a medium content of 30-35 % CaF_2, 35 % SiO_2, 25 % $CaCO_3$ and 2-3 % $BaSO_4$.

The roof of mineralization is impermeable and the faults produce an impermeable barrier that hydraulically independents the three levels of the mine. Faults facilitate water circulation from the surface to the permeable levels, so the inflow water is high, on average 15 litres per second.

Water management is very important for the Moscona mine; each year 400.000 m^3 of water is pumped out of the mine to the Lavares stream.

MINE WATER MANAGEMENT

Mining introduce changes in the aquifers and water table, both in quantity and quality. Workings cause permanent flow of water into the mine and loss of water from aquifers. Mine water analyzed has high total dissolved solids and high fluor ion content.

MINE WATER DRAINAGE

In accordance with the stratigraphic description of materials, it is possible to distinguish three types of sediments on the basis of their permeability:

- Impermeable materials: shale and marls that appear in Palaeozoic series (Rañeces, Moniello, Naranco Formations) and those clay and marl deposits of the overlay Triassic levels.
- Detritic materials with secondary permeability: Shear and fractures lead to secondary permeability in some materials like the lower detritic level of Triassic and the conglomerate section in the upper detritic level. Frequently are very poor aquifers.
- Secondary permeable carbonated materials: Limestone and dolomites and some sandstone with carbonate cement may develop a secondary permeability by karstification and fracturation. At this kind of materials correspond the calcareous Triassic level, where fluorite mineralization is developed and the detritic roof of the mineralized bed.

The water recharge in permeable materials is produce mainly by rain water infiltration although some kind of underground transference process can be possible in the discordant contact between carbonate Palaeozoic sediments of the basement and the Triassic coberture. Natural drainage takes place by means of small springs and by the Albares river and its subsidiaries, one of this is the Lavares stream.

GROUNDWATER CONTAMINATION

The natural concentration of fluoride in groundwater depends on the geology, chemistry, physical characteristics and climate of the area. Generally spring and well water tend to contain higher concentration of fluoride than surface waters from lakes and streams.

In general, the literature suggests that, if water is not in contact with high-fluoride minerals, the range of concentrations are about 0,01 to 0,4 mg/l (Weinstein & Davison, 2004)(3), but even where most water is within this range there may be local areas, like could be the case studied in this paper, where fluorite deposits lead to much higher concentration, considering even that fluoride concentration is a useful indicator of this kind of mineral deposits.

The solubility of fluoride is controlled by equilibrium with CaF_2, but concentration leads to precipitation of calcite ($CaCO_3$) and that increases the solubility of fluoride, hence the concentrations of fluoride are increased with higher temperatures in environment.

Workings in Moscona mine produce an artificial drainage, specially in the zones near the faults. The wall and roof of mineralized bed have a very low permeability as has been descript, so the other contributions come from the calcareous permeable Triassic level.

Mine water quality was studied and ranges of different parameters are given in Table I. Samples have been collected in different points inside and outside the mine. Samples M1 to M8 have been collected in the mining mineralized area (M6-M8 poured water from boreholes), T4 and T5 come from the deepest exploitation level. S3 is a sample from a surface spring and R1 is water from Lavares upstream the mine.

Table I Geochemical characteristics of Moscona Mine Water

	M1	M2	M3	T4	T5	M6	M7	M8	S3	R1
Hardness	605	398	571	49	49	235	301	232	264	232
HCO3+CO3/Ca	1,03	1,02	0,32	11,6	11,7	1,7	0,91	3,04	1,15	1,07
Cl/Na	1,15	1,08	1,3	0,1	0,1	1,22	1,3	1,33	1,15	1,23
SO4/Ca+Mg	3,74	5,69	3,96	46,02	46,02	9,64	9,81	9,81	8,56	9,72
Zn	0,84	2,24	2,68	2,68	2,68	2,68	0,33	<0,05	<0,05	<0,05
Ni	0,32	0,27	0,06	0,06	0,06	0,06	0,02	<0,01	<0,01	<0,01
Fe	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1
F	3	2,5	3	3,5	3,5	2	1,5	0,5	0,5	0,5
DQO	0,6	0,8	0,7	0,6	1	0,8	0,6	1,4	3,1	3,9
pH	7,6	7,7	7,6	8,2	8,1	7,7	7,7	7,7	7,8	7,9
Conductivity	891	638	873	1706	1779	413	509	431	451	405

Geochemical composition of water samples taken inside Moscona mine shown that water in contact with the mineralization has a high salinity degree, with 800-1700 µs/cm conductivity, pH between 7,6 and 8,2 and high fluoride (1,5-3,5 mg/l), sulfate and calcium carbonate content.

It is worth mentioning that the deepest samples present higher fluoride and carbonate concentrations, and in general the highest mineralization levels, perhaps due to the longer residence time of water in the formation, during which important disolution proccesses will have been taken place. The presence of Zn is associated to carbonated rocks.

As a result fluorite mining has caused significant degradation in ground water quality. One special peculiarity of this fluorite field is that the mine water does not have acid mine drainage problem as the mineralized deposits are not associated with pyrites and sulphur content.

SPANISH REGULATION FOR FLUORIDE CONTENT IN SURFACE WATERS

In Spain, as result of application of 76/464/CEE Directive, a new regulation has been approved (RD 995/2000) in order to establish quality targets for some contaminant substances to eliminate contamination in surface water. This regulation establishes for fluoride a limit in the annual medium concentration of 1,7 mg/L.

Under this rule, mining and other industries are complied to get a waste authorization for this kind of substance and need to develop a contamination reduction program with activities and schedule in order to get quality targets.

WATER WASTE IN LAVARES STREAM

Contaminative mine drainage waters have become one hydro geological and geochemical problem arising from mining. Liquid effluents from Moscona underground mine are discharged into the Lavares stream thereby polluting it, producing changes both in quality and flow parameters. Each year approximately 200.000 m^3 of water is pumped out of the mine to the Lavares stream.

Lavares stream has a small basin with a surface of 7 km^2, the main course has about 4 km length, with a height between 384 and 88 meters. The study area is template and has four seasons, with a mean annual rainfall about 1100 mm and a medium temperature of 13,5º (Figure 1).

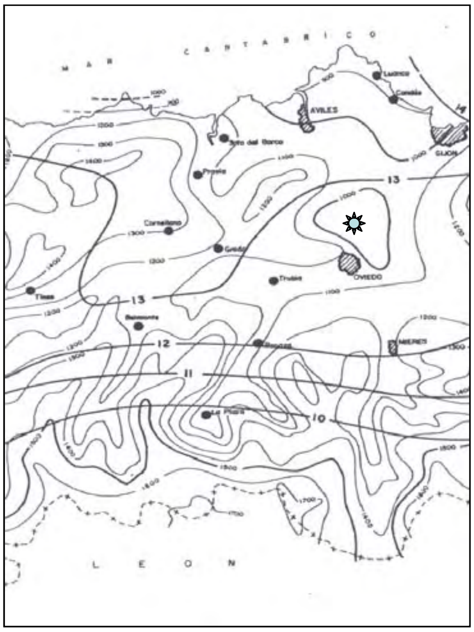

Figure 1. Temperature and precipitations in the study area

There are no direct river volume measurements, but by means of mathematic modelization (Témez, 1978)(4) a volume between 0,8 and 2,6 m^3/s has been estimated for the stream (Table II).

Table II. Daily medium estimated volume for Lavares stream

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Q (m^3/s)	2,14	1,44	1,33	1,31	1,36	1,42	0,79	1,43	1,39	1,99	2,61	1,78

With those data is possible predict that the period in which effluent from the mine may have worse consequence due to pollutants dilution reduction would be July month. This value is used to waste authorization application and to subsequent control.
Water waste from Moscona mine has been analyzed periodically since 1998 (Table III), before being discharged into the Lavares stream.

Table III. Results of analysis of water waste from Moscona mine

Date	**Volume (l/s)**	**Fluoride (mg/l)**	**pH**	**Solids (mg/l)**
26/03/98		4,6	8,2	11
15/06/98		2,9	7,9	6
30/09/98		3,1	7,8	41
14/12/98		0,27	8	63
14/01/99		4,3	7,9	54
12/04/99		3,48	8,9	39
24/08/99	8,3	4,7	7,3	5
27/10/99	7,7	4,5	7,6	24
17/01/00	20,9	4,7	7,4	1
12/04/00	11,7	1	7,5	3
25/07/00	16	3,9	7,9	2
16/10/00	12	3,9	7,7	2
27/03/01	8,9	4,1	8	<2
18/07/01	8,4	4,8	7,3	<2
18/09/01	8,69	3,6	7,6	2
26/11/01	8	4,4	7,4	<2
28/02/02	8,4	3,9	7,5	<2
14/05/02	7,1	3,2	7,7	3
16/09/02	7,6	4,1	7,6	<2
20/11/02	7,5	3,9	7,7	<2
21/03/03	8	2,29	7,62	4
12/06/03	10,9	1,2	7,49	13
15/09/03	8,3	1,29	7,43	10
16/12/03	6,4	1,2	7,48	21
16/03/04	11,1	1,3	7,4	2
14/06/04	11,1	1,45	7,4	1,8
01/09/04	11,1	3,15	7,42	2
10/12/04	6,9	2,5	7,78	2
17/03/05	14,6	3,4	7,6	0,5

As average, a maximum of 10 l/s have been pumped out of the mine. Mine water flooding from the mine has a high content in fluoride, in data before December 2002 higher than 3 mg/l (Figure 2). The water mine pH remain above 7,3 and there is no acid water problem.
There is no relationship observed between pH and fluoride solubility, and changes in fluoride concentration could have origin in the working advances, because when a mining area is opened the water chemistry is changed due to the origin and age of the in-flowing water. Initially, the water that has been stagnant in the rock is drained, and a recharge zone is developed with fresh water entering the zone.
The solids dissolved content has no correlation with water volume pumped or with fluoride concentration.

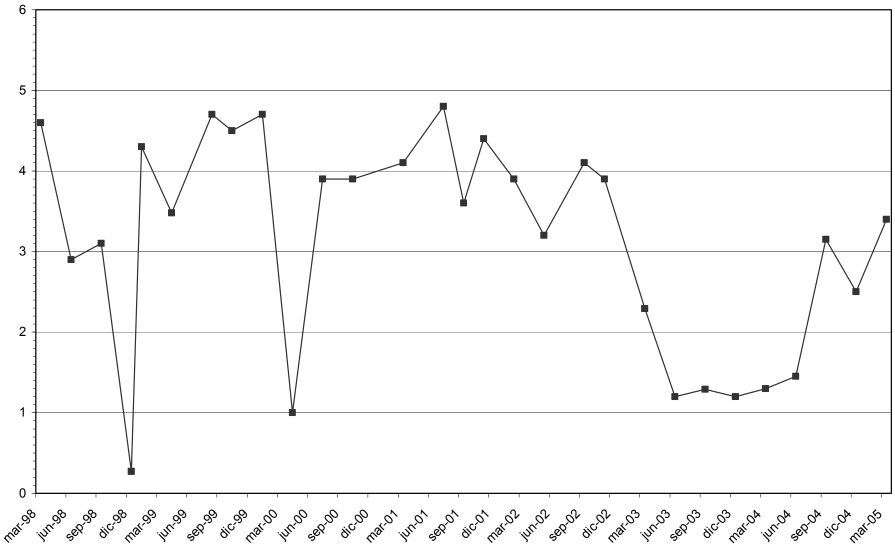

Figure 2. Fluoride concentration (mg/l) in mine water discharged into Lavares stream

MINE WATER TREATMENT

In general, mine water problems may be addressed by isolating the contaminant source, by suppressing the reactions releasing contaminants or by active or passive treatment (Banks, D. et al, 1997)(5).
In Moscona mine the selected method is a passive one: all the drainage water is collected in a decanting pond sited inside the mine before being pumped out to the stream.
In December 2002, a new pond was built in order to increase its capacity and the time water stay in it. The decanting pond has now a huge volume, which allows water a long residence time, of almost one week. The effect of this time increase has produce a notable fluoride reduction enough to guarantee fluoride levels inside the authorization limit values.
The decanting pond allows keep in acceptable levels the solid content levels. All the quality parameters of the water that gets into the river are monitored in a chest build for this purpose.

CONCLUSIONS

The hydrochemistry of water is characterized by enrichment in concentrations of fluoride, calcium carbonate and calcium and magnesium sulphate, in ground and in surface water. High conductivity and hardness of water analyzed revealed a high salinity degree. Changes in fluoride concentration have to be studied deeper because could have relation with the working advances, because when a mining area is opened the water chemistry is changed due to the origin and age of the in-flowing water.
The decanting pond built inside the mine is become an efficient pasive treatment to reduce fluoride and solids content to acceptable limits. Contamination levels are controled in order to get adequate quality parameters in surface water.

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