MINE, WATER & ENVIRONMENT. 1999 IMWA Congress. Sevilla, Spain

# STUDY OF THE IMPACT IN GROUNDWATERS AFTER THE RESTORATION OF AN OLD URANIUM MINE (SPAIN)

**Paloma Gómez, Antonio Garralón, Mª Jesús Turrero, Lorenzo Sánchez, Benigno Ruiz and Francisco Fernández**

CIEMAT
Avda. Complutense, 22. 28040 Madrid, Spain
Phone: +34 91 3466138 , Fax: +34 91 3466542
e-mail: maraje@ciemat.es

## ABSTRACT

*An important effort of uranium mines restoration is being carried out by ENRESA in order to establish the influence of the uranium mineralisation on the groundwater quality, and hence to control the efficiency of the restoration works. The knowledge of the chemical characteristics of groundwater around the mines and the mobilisation/retention processes that control the uranium and heavy metals concentration on natural waters, give key criteria to improve the recovering of similar mines for the future.*

*The "Ratones" mine is situated to the West of Spain (Cáceres) and has been selected for its special characteristics to evaluate the impact of the restoration upon the groundwater system. The host rock of the uranium mineralisation is constituted by a granitic leucocratic facies. The U mineralisation, which was mined in the 70´s, is mainly composed of pitchblende, parapitchblende, iron sulphides and phosphorites. Hydrogeological studies were carried out to determine the preferential flow-paths (NE-SW) of the studied area, and the discharge points of the mine were located. Sixty-one sampling points (from surface waters and springs), located within an area of 200 Km$^2$ around the mine, have been chemically and isotopically characterised. Redox conditions of the waters were guaranteed due to anoxic conditions of the sampling method.*

*The main results obtained show that the redox conditions of the mine water hindered the U mobilisation towards the preferential flow paths. The dissolution of arsenopyrite present in the U mineralisation, is responsible of the presence of arsenic, which is the main indicator of the pollution of the mine. Except for the arsenic concentration, groundwater present unpolluted conditions around the mine.*

## INTRODUCTION

The uranium mine restoration plan, carried out by ENRESA, considers various complementary works to obtain the necessary information about the environmental mine impact that the restoration works can originate in the area, specially on the groundwater. The Ratones uranium mine, due to its characteristics, has been selected to develop an in depth study, in order to obtain the necessary information about the geological characteristics, the regional hydrogeology and the hydrogeochemical characteristics of the surface waters and groundwaters. All this information is necessary to develop a model that can define the environmental impact of the mine.

The Ratones mine was mined by the Junta de Energía Nuclear from 1955 until 1974. Two quartz dykes with massive pitchblende and parapitchblende were exploited. Also, as accompanying mineral, iron sulphurs were detected in great abundance. The deepest gallery excavated was situated at 180 m depth.

The Ratones mine is located in the southern area of the Albalá granitic pluton (Cáceres, Spain), which is classified as a peraluminic granite. Two types of granites associations are differentiated, considering the major and trace elements geochemistry: The association 1 is richer in $Fe_2O_3$, $Na_2O$, $P_2O_5$, Be, B, Cs, V, Zr, Ba and Sr than the association 2, but is poorer in $TiO_2$, $K_2O$, Rb, F, Th and Tr. Also, both have very similar proportions of FeO, MgO, CaO and U.

The regional scale flux model is mainly controlled by topography, a very plain area, except by Sierra de San Pedro (NW-SE direction) and by Montánchez (SW-NE direction), rising between 300m and 500m over the plains. The water boundary between Tajo and Guadiana Rivers is very close to Ratones mine (478m.a.s.l.). The surface discharge points of the Ratones mine are the Maderos stream, and, maybe by more deep fluxes, to the Ayuela River (Martínez, et. al., 1998)

In order to carry out chemical analysis on representative samples, it is necessary to carefully select the sampling points. Hydrogeochemical interpretation of the system would not be complete if it did not include the information provided by the natural surface waters, since these give rise to the initial waters, which percolate through the geological media evolving to the groundwaters. The seasonal hydrochemical characterisation of the springs and fountains has been one of the objectives most clearly accomplished within the framework of the study. Insight has been gained into the geographical location of the possible discharge point of the system due to the great importance that these points have in environmental impact studies. Overlapping the structural information on the system and the co-ordinates for the springs has allowed important progress to made the hydrochemical and hydrogeological interpretation of the pluton.

## SAMPLING METHOD

Waters samples were taken using a low flow-rate electric pump connected to a generator. In this system the water passes through a 0.45 microns tangential cartridge to a continuous flow cell electrode of a geochemical multiprobe (Hydrolab H20) until the stabilisation of the physico-chemical parameters is achieved. The flow cell is a closed system in order to prevent oxidation processes and $CO_2$ exchange with the atmosphere.

The geochemical multiprobe allows the continuous monitoring of the pH, Eh, electrical conductivity, $O_2$ and temperature.

All the samples were filtered by 0.45 µm. The sample preservation changes according to the particular constituents being determined. In this way, samples for determination of cations and heavy elements were acidified with ultrapure nitric acid to pH < 1.5; sulphuric acid was used in samples for the determination of dissolved organic carbon and $NH_4^+$; samples collected for $Fe^{2+}$ and $Fe^{3+}$ were acidified with ultrapure hydrochloric acid to pH < 1.5; non-acidified bottles were kept for the determination of anions and silica. The samples were transported to the laboratories in a thermostatic box at a temperature of 4ºC.

## ANALYTICAL TECHNIQUES

The common anions ($Cl^-$, $Br^-$, $NO_3^-$, $NO_2^-$, $PO_4^{3-}$, and $SO_4^{2-}$) were analysed by ion chromatography (U.S. EPA Method 300.1). An ion chromatograph Dionex 4500i was used. The determination of Na, Li and K was performed by flame emission spectroscopy using an atomic absorption spectrometer Perkin Elmer 2280 (A.P.H.A., AWWA & W.E.F., (1995). Main cations and some trace elements were determined by inductively coupled plasma- atomic emission spectrometry (ICP-AES). Trace and ultratrace elements were determined using a Finnigan MAT SOLA quadrupole ICP-MS. The methods were validated with certified reference materials of the Community Bureau of Reference (BCR) of the Commission of the European Communities.

Fluoride, iodine and ammonia were determined by potentiometry, with Ion Selective Electrodes (A.P.H.A., AWWA & W.E.F., 1995). Alkalinity was determined by potentiometric titration with inflection point detection in a Titroprocessor Methrom 670. Total silica was determined with the ammonium molybdate colorimetric method (U.S. EPA Method 370.1), whereas Fe(II) and total Fe were analysed by the Ferrozine colorimetric method (ASTM, 1981). An UV-Vis spectrophotometer Beckman DU-7 HS equipped with 1 cm path quartz cells was used. Total organic carbon was determined by Combustion and Infrared detector Method in a TOCOR analyser (Maihac- Westinghouse) (U.S. EPA 415.1)

## RESULTS AND DISCUSSION

To characterise the area 61 sampling points (springs, wells, boreholes, etc.) were selected, in order to obtain information of the hydrogeochemical parameters of the groundwaters. A seasonal sampling was made to verify the variations originated in the chemical composition and to detect the permanence of the sampling points. All the non-permanent sampling points were discarded.

A principal components analysis has been made, in order to determine the variables related with the hydrogeochemical processes involved in the water evolution. Previously, all the data were normalised, and the SPSS v. 6.01 code was used (Norusis, 1994). Three components were obtained, explaining 85.5% of variability:

Component 1= $Cl + Mg + SO_4^{2-} + Na + Sr + Ca + SiO_2$
Component 2 = $As + Mn + Fe^{2+} + HCO_3^-$
Component 3 = $K + NO_3^-$

In Figure 1 a representation of the two principal components is shown. Component 1 represents the chemical composition of waters located in shales (1129-8-2043 and 2044, SE area, $Cl\text{-}SO_4^{=}\text{-}Mg$ waters), clearly differentiated of granitic sampled waters.

Component 2 indicates the environmental impact of the mine wells, especially the As content. The origin of As in waters is probably due to the arsenopyrite present in the U-dyke. It is significative the Mn and Fe association in this component due to the fact that sulphides, specially pyrite, is present in the mineralised dykes in a great amount. The sample 1129-8-1012 is a mine well whose As content is higher than the rest of the samples, even the rest of the mine wells

Component 3 represents the polluted waters with nitrates. Sampling points 1129-8-1026 and 1129-8-2041 are two wells of 55 m and 40 m deep respectively, located in a farm and their pollution is mainly due to fertilising and cattle industry.

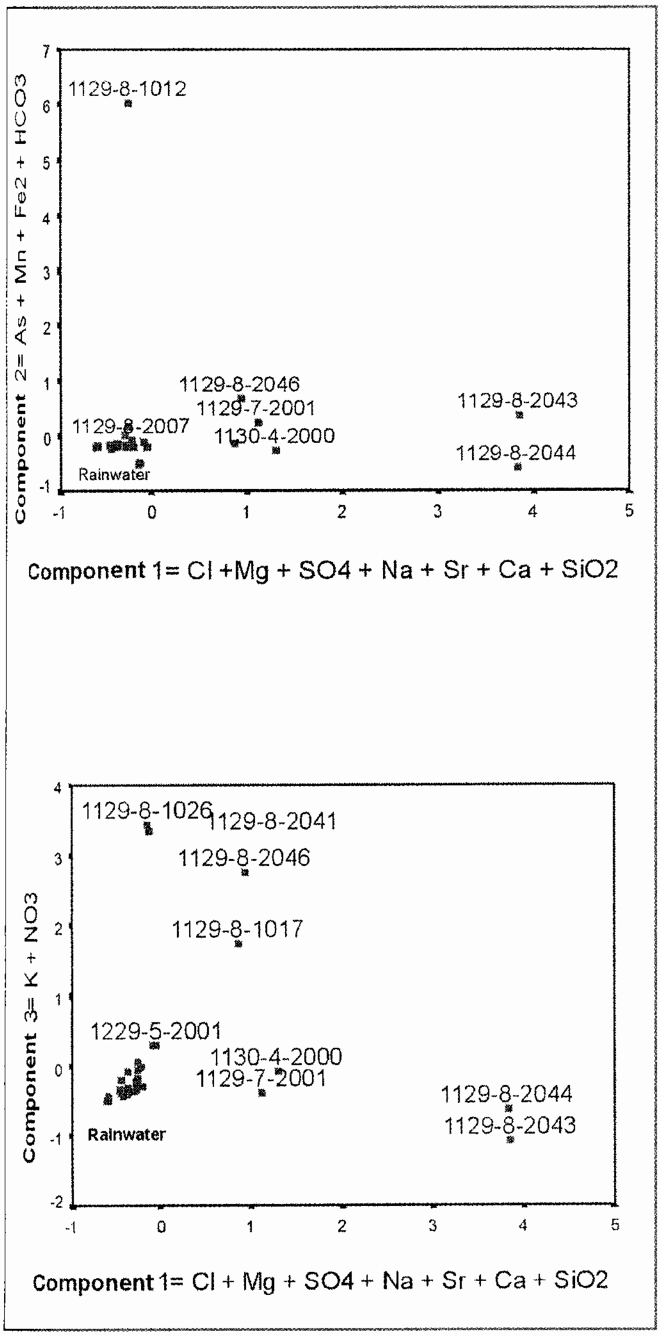

Figure 1.- Component 1 versus component 2 and component 1 versus component 3 in the surface waters of the Ratones mine.

A general classification of the waters based on physicochemical parameters and their chemical composition has been carried out. Four major groups has been differentiated. The groups are clearly correlated with the litology (granites and shales) and its location respect to the mineralised dykes (Figure 2):

- Shales: These waters show a high content of $Cl^-$, $SO_4^=$, Ca, Mg and Na respect to the rest of the samples.
- Mine wells: The waters located in the mine wells are Mg-Ca-$HCO_3$. The origin of sulphates in these waters is due to the sulphide oxidation from the mineralised dykes.
- Mine influence: This group is formed by $HCO_3$-Na type waters and are located close to mine wells.
- Maderos stream: This group of waters are $HCO_3$-Na-Ca type and are located at both sides of Maderos stream, the natural surface discharge of the Ratones U-mine.

The previous classification has been made considering the major ions of the waters, but if the $^3H$ values are considered, then some differences are observed in the groups. The samples located in shales show differences in residence time (Figure 2). The named group "young shales" is $HCO_3$-Cl-Na type and the called "old shales" is $SO_4$-Cl-Mg type.

The rest of the groups show a very similar tritium contents, typical to recharge waters ($^3H$ mean content in rainwater 5,17±0,5).

Only one sampled water showed tritium values close to zero (1129-8-1006). Due to its characteristics as a possible discharge point, a new group was created and identified as "old water".

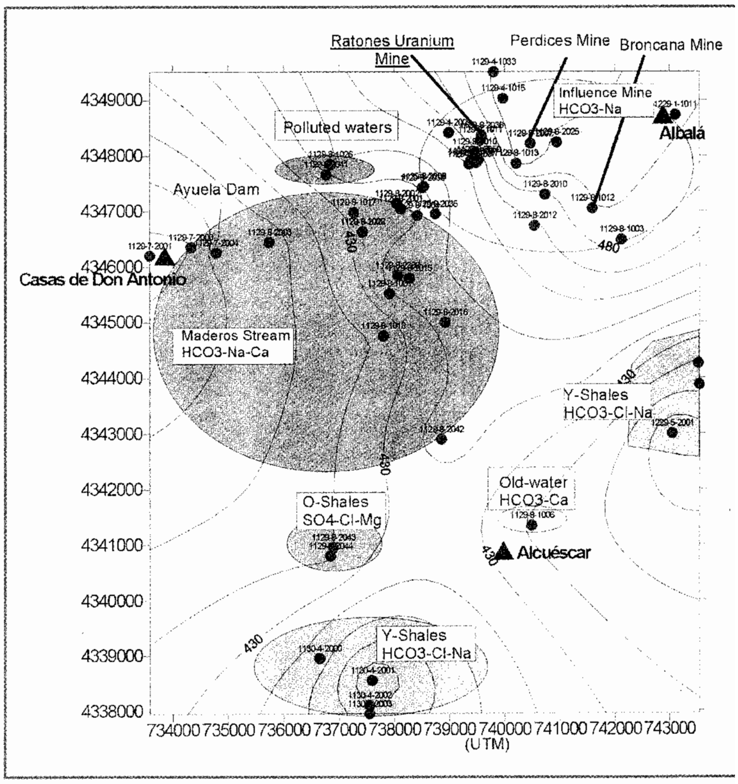

Figure 2.- Geographical situation of the groups of water from the Ratones mine.

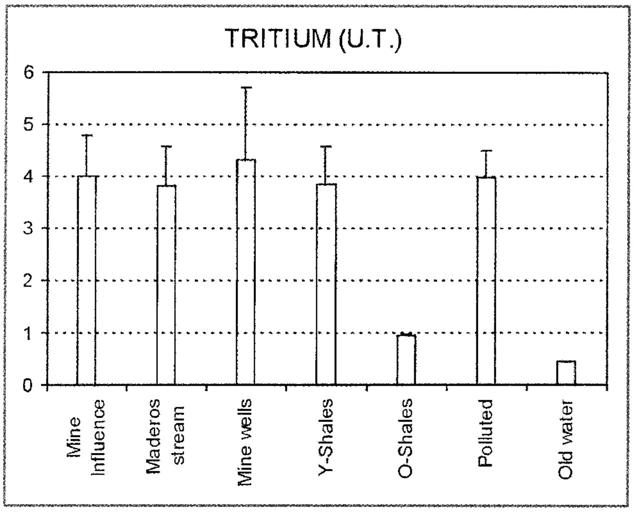

Figure 3.- Tritium mean content in the different groups of samples from the Ratones mine environment.

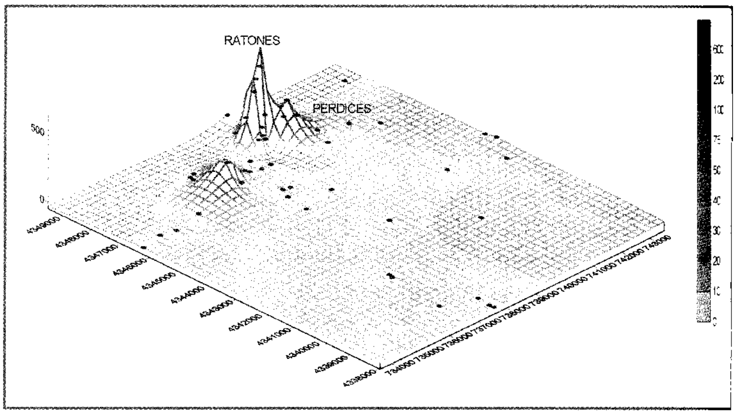

Figure 4.- Spatial distribution of the arsenic concentration (ppb) in the Ratones mine surrounding. The X and Y axis represents the UTM coordinates and the Z axis represents the As concentration in the samples.

In Table 1 are given the analytical results of the mean chemical composition from each groups of waters. The waters show values of pH between 5.4 and 7.6. The mine wells show lower values of redox potential (Eh) than the rest of the waters. It is remarkable the high electrical conductivity measured in the polluted waters and in the samples from the group of old shales.

As was noticed in the statistical study, the mine impact over the surrounding waters is mainly due to the high arsenic content. In the mine wells the mean concentration is 535 ppb with a standard deviation very high as is reflected in Table 2. The higher determined concentration has been 820 ppb and the lower 25 ppb. These differences are mainly due to the variation of the presence of arsenopyrite in the U-mineralised dykes. The spatial distribution of dissolved arsenic is represented in Figure 4. The maximum values are associated to the wells corresponding

| | **Mine Influence** | | **Maderos stream** | | **Mine wells** | | **Y. shales** | | **Old shales** | | **Polluted** | | **Old** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Std.dev. | Mean | Std.dev | Mean | Std.dev | Mean | Std.dev | Mean | Std.dev | Mean | Std.dev | Mean | Std.dev |
| Ce(uS/cm) | 85,29 | 39,08 | 139,27 | 124,67 | 622,55 | 221,39 | 357,64 | 237,33 | 1646 | 521,22 | 1318,7 | 830,31 | 257,5 | 36,06 |
| pHin situ | 7,18 | 1,54 | 6,45 | 0,86 | 6,98 | 0,74 | 6,52 | 0,61 | 6,03 | 0,26 | 5,4 | 0,17 | 7,6 | 0 |
| Eh (mV) | 334,18 | 101,65 | 365,35 | 77,52 | 179,38 | 57,59 | 283,2 | 80,88 | 324 | 99,45 | 485 | 65,83 | 425 | 16,97 |
| $HCO_3$(mg/l) | 26,81 | 16,69 | 31,68 | 10,91 | 191,65 | 123,11 | 110,64 | 72,41 | 43,98 | 14,23 | 18,4 | 9,09 | 116 | 8,49 |
| F(mg/l) | 0,2 | 0,12 | 0,13 | 0,04 | 1,24 | 0,71 | 1,07 | 1,92 | | | 0,2 | 0,1 | 1,4 | 0,14 |
| Br(mg/l) | 0,09 | 0,03 | 0,1 | 0,02 | 0,1 | 0 | 0,22 | 0,2 | 0,31 | 0,24 | 0,1 | 0 | 0,06 | 0,06 |
| Cl(mg/l) | 10,12 | 6,78 | 7,55 | 5,06 | 11,76 | 11,12 | 61,4 | 31,93 | 230,5 | 98,05 | 34,33 | 4,93 | 14 | 1,41 |
| $NO_3$(mg/l) | 0,89 | 1,57 | 1,72 | 2,02 | 0,38 | 0,46 | 0,79 | 0,93 | 1,8 | 1,47 | 99,33 | 8,02 | 0,1 | 0 |
| $PO_4$(mg/l) | 0,32 | 0,26 | 0,41 | 0,73 | 0,37 | 0,51 | 0,41 | 0,48 | 0,1 | 0 | 0,1 | 0 | 0,14 | 0,05 |
| $SO_4$(mg/l) | 1,71 | 1,32 | 5,57 | 4,83 | 89,13 | 53,94 | 39,8 | 20,44 | 459 | 165,04 | 15,33 | 3,79 | 19,5 | 2,12 |
| Ca(mg/l) | 2,87 | 1,5 | 5,71 | 2,94 | 38,88 | 12,57 | 16,42 | 5,69 | 81,25 | 32,57 | 25,33 | 6,66 | 33,5 | 3,54 |
| Mg(mg/l) | 1,04 | 0,62 | 2,11 | 1,38 | 25,93 | 16,95 | 20,44 | 13,65 | 118 | 44,82 | 6,17 | 0,81 | 6,15 | 0,64 |
| Na(mg/l) | 11,49 | 5,01 | 9,18 | 3,65 | 28,38 | 14,27 | 47,4 | 31,4 | 101 | 40,21 | 23 | 4,36 | 19 | 1,41 |
| K(mg/l) | 2,74 | 3,36 | 1,58 | 1,3 | 5,74 | 6,27 | 2,2 | 1,08 | 2,63 | 0,49 | 14,03 | 7,75 | 1,15 | 0,07 |
| Li(mg/l) | 0,01 | 0 | 0,01 | 0,01 | 0,11 | 0,15 | 0,07 | 0,08 | | | 0,03 | 0,02 | 0,12 | , |
| U(ppb) | 2,53 | 1,81 | 2,96 | 3,77 | 21,63 | 12,05 | 1 | 0 | 1 | 0 | 291,33 | 434,46 | 1 | , |
| TOC(mgC/l) | 3,88 | 3,13 | 6,13 | 2,16 | 11,2 | , | 3,5 | 0,57 | 0,9 | 0,42 | 2,95 | 0,07 | 1,1 | , |
| $SiO_2$(mg/l) | 21,07 | 7,69 | 14,45 | 5,37 | 17,6 | , | 28,7 | 10,18 | 36,55 | 3,89 | 22,7 | 0,71 | 38,6 | , |
| $NH_4$(mg/l) | 0,1 | 0 | 0,11 | 0,03 | 0.21 | , | 0,1 | 0 | | | 0,1 | 0 | 0,13 | 0,04 |
| Tritium(T.U.) | 4,01 | 0,78 | 3,82 | 0,76 | 4,32 | 1,38 | 3,84 | 0,74 | 0,94 | 0,04 | 3,98 | 0,52 | 0,45 | , |
| Al(mg/l) | 0,09 | 0,04 | 0,08 | 0,04 | 0,05 | , | 0,05 | 0 | | | 0,16 | 0,03 | 0,05 | , |
| As(ppb) | 18,67 | 10,84 | 13,49 | 9,75 | 535 | 442 | 4 | 0 | 4 | 0 | 15,5 | 0,71 | 18 | , |
| Sr(ppb) | 30 | 0 | 33,68 | 8,31 | 220 | , | 190 | 84,85 | 560 | 14,14 | 100 | 0 | 90 | , |
| Zn (ppb) | 31,67 | 4,08 | 33,16 | 9,46 | 30 | , | 515 | 558,61 | 30 | 0 | 45 | 21,21 | 30 | , |
| Mn(mg/l) | 0,15 | 0,29 | 1,65 | 6,87 | 0,18 | , | 0,2 | 0,08 | 0,7 | 0,29 | 0,1 | 0,03 | 0,14 | , |

Table 1. Mean chemical composition of the different groups of waters.

to Ratones U-mine and Perdices U-mine. The value decreases immediately in the surroundings of the mines, being observed only a point with values significantly higher than the rest. However, this point is located in a 70 m well, connected with an non-mined uranium dyke.

The trace elements concentrations in the mine wells are represented in the Table 2. These elements are very significant in order to evaluate the environmental impact of the mine over the surrounding groundwaters. The heavy metals concentrations determined in the mine wells are below 50 ppb, except Sr. It is remarkable the low concentration of dissolved uranium. At reducing conditions and near neutral pH, the solubility of uranium is very low and there is little concern for the release.

| | **Mean** | **Std. dev.** |
|---|---|---|
| U (ppb) | 21,63 | 12,05 |
| As (ppb) | 535.0 | 442,69 |
| Ba (ppb) | 46 | 14,42 |
| Be (ppb) | 20,11 | 17,14 |
| Bi (ppb) | 76,7 | 107,82 |
| Cd (ppb) | 20,17 | 17,19 |
| Co (ppb) | 38,33 | 20,21 |
| Cu (ppb) | 24,33 | 9,81 |
| Mo (ppb) | 21,23 | 15,18 |
| Ni (ppb) | 21,17 | 15,3 |
| Pb (ppb) | 33,87 | 28,81 |
| Th (ppb) | 0,12 | |
| Sr (ppb) | 220 | , |
| Zn (ppb) | 30 | , |
| Mn (ppm) | 0,18 | , |

Table 2. Trace elements mean chemical composition in waters of the mine wells.

## CONCLUSIONS

A restoration plan has been carried out in the Ratones U-mine. The environmental impact of the mine over the preferential flow path has been evaluated.

The reducing conditions in the waters from mine wells hinder the U mobilisation, originating unpolluted discharge waters from the mines.

Arsenic can be considered as a tracer of the mines pollution, due to its origin from the U-mineralised dykes. This element can be used to indicate the environmental impact originated by the mine wells in the surrounding groundwaters. However, the high concentrations measured in some mine wells (850 ppb) never reaches the maximum limit allowed by the Spanish Law (1000 ppb). The dissolved arsenic content in the waters surrounding Ratones mine ranges 3 from 28 ppb, which indicates that the pollution from the mine wells do not originate an appreciable environmental impact in the surrounding groundwaters.

## ACKNOWLEDGEMENTS

The chemical analyses were carried out in the laboratories of the Analytical Chemical Department in CIEMAT. We wish to thank Berta de la Cruz for her comments and suggestions, as well as Pedro Rivas (CIEMAT), whose technical comments and revision were greatly appreciated. We would like also to especially thank the Empresa Nacional de Residuos Radiactivos, S. A. (ENRESA).

## REFERENCES

A.P.H.A., AWWA and W.E.F., 1995. Standard Methods for the Examination of Water and Wastewater. 19th ed. American Public Health Association, Washington.

ASTM Part 31 on Water, p. 445, method D-1068 part A, 1981.

Drever, J.I., 1988. The geochemistry of natural waters. Prentice Hall Inc. Engkewood Cliffs, New Jersey.

Garrels, R.M., 1967. Genesis of some ground waters from igneous rocks. Researches in Geochemistry 2, John Wiley and sons, N.Y., 405-420.

Martínez, L., F. Ortuño and K. Bitzer. Modelo hidrogeológico regional. 10-UPC-IA-04-02.

Norusis, M.J., 1994. SPSS Advanced Statistic 6.1, SPSS Inc. USA.

Stumm, W., and J. J. Morgan, 1981. Aquatic chemistry. John Wiley & sons, inc.

U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, 1991. Methods for the determination of metals in environmental samples. Rep. EPA/600/4-91/010, June 1991.