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Evolution of Different Redox Couples During the Weathering of Mine Waste

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A temporal and spatial hydrogeochemical monitoring programme has been carried out on waters draining a waste heap at the former gold mine of Chéni, France (Bodénan *et al.*, 2000). The main water-rock interaction process corresponds to oxidation of pyrite and arsenopyrite traces in the heap. Particular emphasis has been placed on studying the behaviour of various redox couples. Based on speciation calculations, the aim was to identify the couple(s) that may influence the redox potential of the environment. The software program used was EQ3NR (Wolery, 1992), the database of which was extended by Gaskova *et al.* (1999) to include minerals and aqueous species of arsenic.

Redox potential and speciation were measured *in situ* before sampling (Bodénan *et al.*, 2000). The redox couples analysed were Fe^{II}/Fe^{III}, As^{III}/As^{V}, S^{IV}/S^{VI} and N^{-III}/N^{V}, and the results show that these were generally in thermodynamic disequilibrium in natural aqueous solutions (Lindberg and Runnells, 1984; Criaud and Fouillac, 1986). It should be noted, in the case of Chéni, that the spatial evolution of the calculated redox potential for each couple is similar to that of the measured redox potential (Fig. 1). This observation concerns both oxidation and reduction processes. In the upstream part of the site (pz1), the waters become progressively oxidised down to the saturated zone (pz2) of the second terrace where oxidation reaches its maximum. Similarly, all the measured redox couples reflect a clear oxidation trend. The measured Eh values decrease downstream of the saturated zone (pz5 and pz3). Higher Eh values were recorded near the river (pz4). Again, all the redox couples reflect to varying degrees the variations recorded by the measured redox potential of groundwater. The measured redox potential variations are everywhere higher than those calculated for the different redox couples, except for iron, which shows a greater deviation at point bbt (Fig. 1). The global impression is nevertheless that the dynamics suggested by the redox potential of the solution are higher than those represented by the different redox couples.

Two groups of redox couples are defined. The first corresponds to couples tending towards oxidising conditions, namely Fe^{II}/Fe^{III} and N^{-III}/N^{V}. Concerning the most oxidising conditions (pz2), the Eh values obtained on the basis of iron speciation suggest equilibrium of the Fe^{II}/Fe^{III} couple. Even under such conditions of partial equilibrium with respect to iron, the measured potential remains different from the speciation results. The few measurements for the N^{-III}/N^{V} couple suggest more oxidising conditions.

The second group of redox couples reflects less oxidising - more reducing conditions, and is represented by As^{III}/As^{V} and S^{IV}/S^{VI}. As for the case of iron demonstrated by the first group, arsenic shows redox equilibrium in the waters of pz2. Nevertheless, the measured Eh values remain distinct from those of As^{III}/As^{V} equilibrium.

In a context of oxidation of mine waste, it is difficult to attribute the redox potential measurements to a specific couple, despite the observation of the partial equilibrium of certain couples (Fig. 1). The only area where the iron data may coincide with the measured Eh values is at the point of maximum oxidation (pz2). The Fe and As concentrations in the waters show a minimum that would correspond to the precipitation of iron hydroxides accompanied by adsorption/co-precipitation of arsenic. It is clear that redox disequilibrium, increasingly detected in natural and anthropic aqueous systems, needs to be taken into account in models of reactive transport (Azaroual *et al.*, 2000).

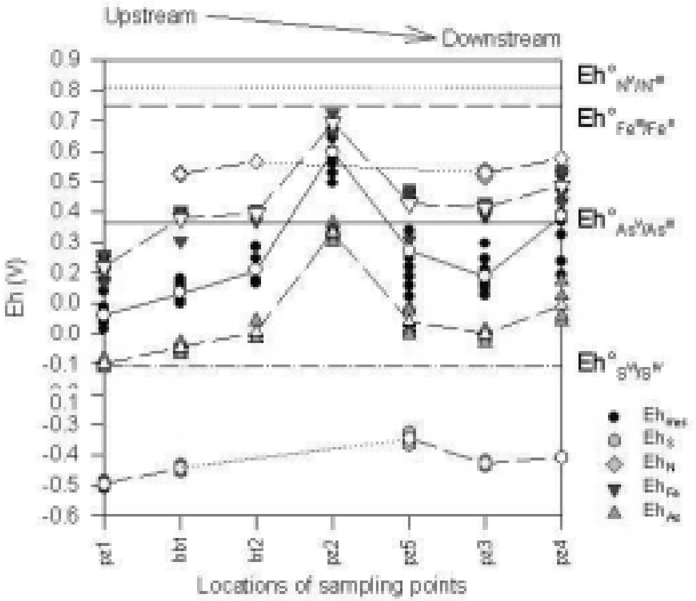

Figure 1: Measured, calculated and theoretical redox potentials, as a function of sampling location, from upstream to downstream of the waste deposit. Calculated redox potentials are obtained from measured speciations.

Bodénan F, Gaucher E, Baranger P, Piantone P & Braibant G, *Proceedings Goldschmidt 2000*, (2000).

Wolery TJ, *EQ3/6 Software Package*, (1992).

Gaskova O, Azaraoual M & Piantone P, *BRGM Report*, **R40629**, 33 p., (1999).

Lindberg RD & Runnells DD, *Science*, **255**, 925-927, (1984).

Criaud A & Fouillac C, *Geochim. Cosmochim. Acta*, **50**, 525-533, (1986).

Azaroual M, Lassin A, Piantone P & Gaskova O, *Proceedings Goldschmidt 2000*, (2000).