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Effect of Phosphogypsum Released Solution on Soil and Aquifer Water

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This paper reports the interaction between natural environment and phosphogypsum free solution hereafter named industrial effluent. It is a strongly acid solution containing some heavy metals and fluorides (F^-). Two components of the receiving environment were considered, ground sediments and Jeffara aquifer water (Tunisia Gabes area). The selection of these two components is linked particularly to their basic character and their phase's differences (liquid and solid). In fact, the considered soil is slightly carbonated and Jeffara aquifer water is slightly basic. In addition, the soil is constituted of various sizes solid particles and could constitute well adsorbent to metal ions existing in phosphogypsum free solution. This effluent contains many ions such as Cd^{2+} and F^- which may react with natural environment after first contact. The experimental study was conducted at room temperature and variable pH to highlight the partition of considered ions between the liquid phase (effluent), the sediment and the potential newly formed solid phase (co-precipitation). This work shows particularly the precipitation of a solid phase identified as CaF_2. It contributes first of all to F^- decrease and then to Cd^{2+} partial removal from industrial effluent which becomes roughly neutral. Consequently it is expected that the effect of this effluent on natural environment will be horizontally restricted and with no vertical expansion due to pH neutralization and ions species retention.

Key Words: Phosphogypsum free solution, Neutralization, CaF_2 precipitation, Cadmium removal.

INTRODUCTION

Phosphoric acid production process leads to the rejection of 1.7 tons of phosphogypsum per ton of treated phosphate rock, which corresponds to 5 tons of phosphogypsum per produced ton of P_2O_5[1]. This residue ranks in the category of hazardous and toxic wastes[2]. Even after washing, the residue remains impregnated with an acid solution[3] whose pH is between 2 and 3. Phosphogypsum also contains impurities from phosphate rock[1-5] such as cadmium and fluoride. Consequently, there are environmental risks associated with phosphogypsum storage methods. In reality, during its storage phosphogypsum liberates a part of its impregnation water. This industrial effluent is highly acidic and contains some ionic entities that may affect natural environment (soil and ground water). The previous observations encourage us to investigate the interaction between natural environment and phosphogypsum free solution hereafter named industrial effluent.

In this context, several authors mention metals ions adsorption by sediments. Zhou *et al.*[6], argue that river sediments adsorb the majority of heavy metals ions contained in rivers water. Several authors[7,8] studied the adsorption of heavy metals ions in rivers or soil sediments. It has been shown that pH is an influencing factor for adsorption. Other works have focused on fluoride removal from wastewater under calcite action[4]. It has been shown in particular the precipitation of CaF_2 and the decrease of Cd^{2+} concentration in the studied solution[4]. Authors attribute Cd^{2+} concentration decrease to simultaneous adsorption and precipitation as otavite ($CdCO_3$). In order to clarify the impact of industrial effluent on natural environment, soil sediments and Jeffara aquifer water (Gabes area, Tunisia) are considered. This option is justified by means of slightly basic characters of the two milieus. Accordingly, acid base reactions can take place between the studied solution and the two retained natural medium representatives.

This work was done at laboratory scale, it has been established that the contact effluent/ground earth leads to the decrease in F^- and Cd^{2+} concentrations also the interaction between Jeffara aquifer water and industrial effluent conducts to the formation of a solid precipitate (CaF_2). The freshly prepared CaF_2 seems to be a good adsorbent to Cd^{2+} ions.

EXPERIMENTAL

The implemented chemical analysis techniques are atomic absorption (ASS VARIO 6 model Analytik Jena, Germany) for alkaline, alkaline earth and cadmium, potentiometry for chlorides (TITRINO DMS 716 of Metrohm), gravimetry for sulphates, pH measurements for pH, ionometry for fluorides (781 pH/ion meter of Metrohm provided with a crystalline membrane electrode 6.0502.150.) and calcimetry is used for carbonate in soils. X-Ray diffraction XRD (PHILIPS-PW 1730/10) is used for solid phase characterization.

Methodology: Due to high acidity of industrial effluent and the diversity of its ionic contents (Table-1), we opted neutralization study. For this purpose, Jeffara aquifer water (Table-1) and soil sediments of the upper layer are used.

TABLE-1
CHEMICAL COMPOSITION (g L^{-1}) OF SOLUTIONS

Designation	Industrial effluent	Jeffara water
pH	2.640	7.95
Conductivity (ms)	15.170	4.89
Density	1.018	1.002
Dry residue	19.981	3.41
Cl^-	0.834	0.88
F^-	1.840	0.003
SO_4^{2-}	3.723	1.26
PO_4^{3-}	3.310	0.004
HCO_3^-	–	0.09
K^+	0.147	0.06
Na^+	3.033	0.64
Ca^{2+}	1.643	0.38
Cd^{2+} (mg L^{-1})*	0.67	0.19
Mg^{2+}	0.511	0.10

*Direct analysis.

Consequently two cases are investigated: liquid/liquid and liquid/solid interactions. In case of liquid/liquid interaction, adopted procedure consists in separating any possible solid suspension by filtering the industrial effluent and after that studying the pH changing as a function of Jeffara aquifer water added volume. Hence, a mass balance is done to determine the ions (Cd^{2+}, F^-) transfer from liquid phase to solid one if any precipitate appears.

In case of liquid/solid interaction, contact leads to a reaction between soils carbonate fraction and acidic solution (industrial effluent). Such neutralization makes probable the formation of a precipitate, therefore adsorption of some ions on newly produced solid phase becomes potential and facilitates ions transfer from the liquid side towards the solid one. In order to elucidate such questions, 15 g of soil and 200 mL of industrial effluent are put together for 70 days without agitation. This option is adopted in order to simulate phosphogypsum storage conditions. Finally solid/liquid mixture is filtered and solution chemical analysis performed. After that a mass balance is completed. The final solid phase is identified by XRD.

RESULTS AND DISCUSSION

Raw materials: The studied solutions are industrial effluent and Jeffara aquifer water (Gabes area southern Tunisia). Investigated soil sediments are sampled from the upper layer in the same area, they are designated SOL_1 to SOL_6. Solutions samples are chemically analyzed (Table-1). Carbonate rates in studied sediments (SOL_1 to SOL_6) are shown in Fig. 1.

Table-1 shows that the industrial effluent is a highly acidic solution (pH = 2.64). Therefore, it is outside the permitted limits, regardless of the receiving medium type: maritime public domain, hydraulic public domain and public pipes.

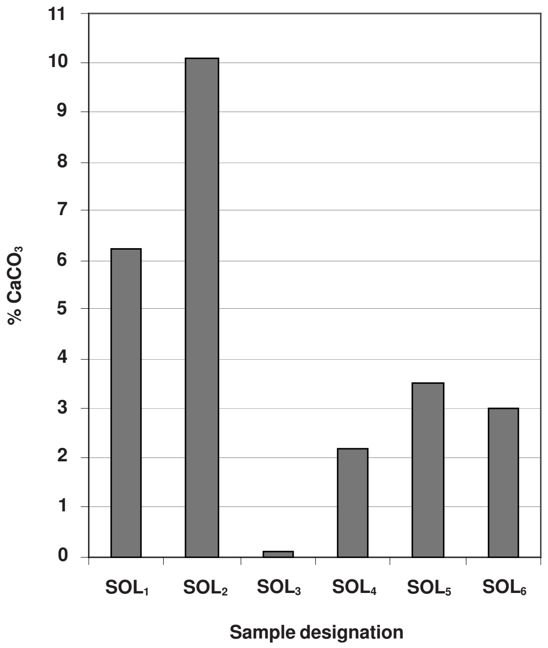

Fig. 1. Sediments carbonate rates

It is also to be noted that fluoride and cadmium concentrations exceed Tunisian allowed standards (NT.106.002/ 1989).

Industrial effluent/sediments interaction: Soil samples and industrial effluent were reacted at ambient temperature for 70 days without stirring. Chemical analyses were carried out on liquid phases before and after interaction (Table-2). The interaction leads to almost total disappearance of carbonates from solid phases (Table-3).

In addition, pH remains acidic whatever the soil sample in question. However a slight increase in pH due to carbonates dissolution is to be mentioned. Fig. 2 shows that pH increases in the solutions after interaction between solid and liquid phases. Such raise is closely linked to initial carbonate rate in soil. A pH maximum was recorded for sample SOL_2, this observation is attributed to calcium carbonate maximum rate.

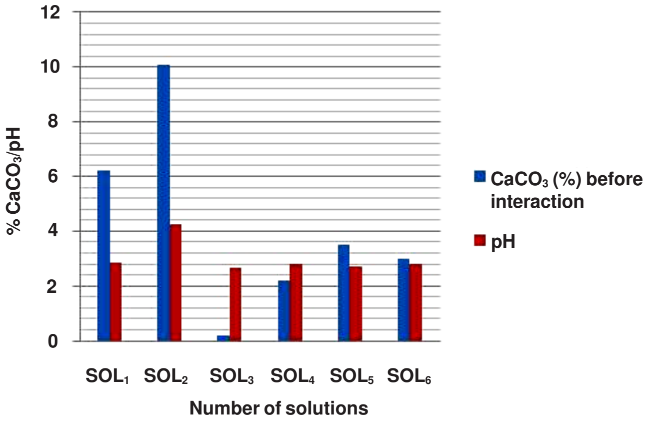

Fig. 2. Industrial effluent pH changing of ($CaCO_3$)

High content of $CaCO_3$ and consequently pH increase, cause a sharp decrease in fluoride concentration in the solution

TABLE-2
LIQUID PHASE CHEMICAL ANALYSES BEFORE AND AFTER INTERACTION WITH SOILS (mg/L)

	Industrial effluent before interaction	Industrial effluent after interaction with soils					
		SOL_1	SOL_2	SOL_3	SOL_4	SOL_5	SOL_6
pH	2.31	2.86	4.24	2.66	2.79	2.70	2.80
Fe	1.74	1.54	0.06	1.26	2.09	2.13	1.75
Na	3161	3510	2661	9456	6444	3381	3741
Al	0.0	13.97	0.04	3.83	8.81	28.1	5.74
Cr	1.76	1.28	0.90	1.36	1.41	1.42	1.32
Zn	3.64	3.67	1.08	4.15	3.83	3.92	5.36
Ca	770	186	165	360	278	253	277
Mg	137	398	440	905	632	84	93
K	71	10	10	10	10	11	11
SO_4	2900	4600	5300	8400	5300	4400	3500
PO_4	3290	2690	1315	2836	2934	2807	2792
Si	1085	520	720	455	440	515	400
Cl	856	898	1055	1048	1020	1005	1005
F	2900	360	30	1000	1000	800	900
Cd	0.5	0.40	0.20	0.40	0.40	0.50	0.40

TABLE-3
CARBONATES ANALYSIS IN THE SOIL AFTER INTERACTION

Designation	SOL_1	SOL_2	SOL_3	SOL_4	SOL_5	SOL_6
$CaCO_3$ (%) before interaction	6.2	10.1	0.2	2.2	3.5	3.0
$CaCO_3$ (%) after interaction	0.0	0.0	0.0	0.0	0.0	0.0

as shown in Fig. 3. Cd^{2+} content remains almost constant at low pH-3. It undergoes after that a decrease of about 60 % when pH exceeds 4 in the industrial effluent as illustrated in Fig. 4.

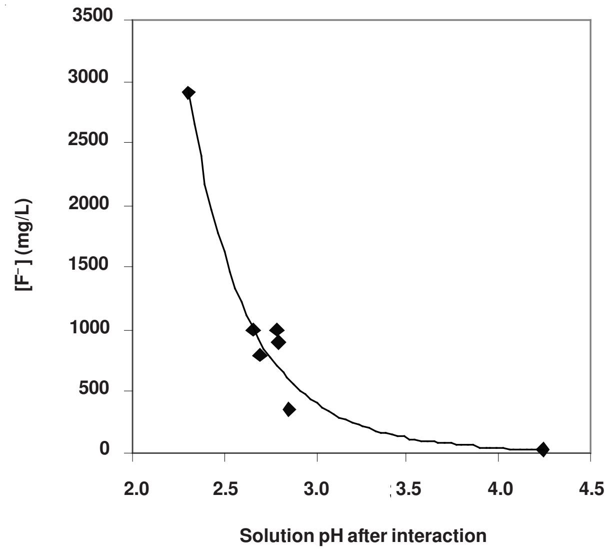

Fig. 3. [F^-] changing in the industrial effluent of (pH)

Industrial effluent/Jeffara aquifer water interaction: A volume of 500 mL of Jeffara water (previously filtered) is employed to study the evolution of pH depending on effluent added volume (Fig. 5). Neutralization causes the precipitation of a solid phase and its XRD identification shows that it is calcium fluoride (Fig. 6).

Changes in Cd^{2+} and F^- concentrations in the filtrates as a function of pH were recorded. Results for F^- were assigned in Fig. 7.

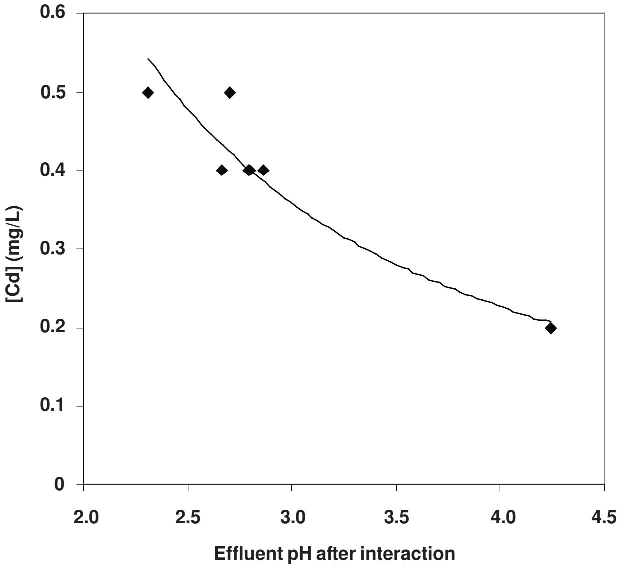

Fig. 4. [Cd^{2+}] changing in the industrial effluent of (pH)

A balance between entering and outgoing cadmium was carried out for each studied solution. The following equations show how the balance was implemented and Dif. Cd (or retained Cd) was plotted as a function of pH variations (Fig. 8).

$$\text{Dif. Cd} = Cd_{in} - Cd_{out}$$

$$Cd_{in} = Cd_{eff.} + Cd_{water\ tested}$$

with $Cd_{eff.} = [Cd]_{eff} * V_{eff.}\ 10^{-3}$ and $Cd_{watertested} = [Cd]_{watertested} * V_{Jeffara}\ .10^{-3}$ and % Dif. Cd = $(Cd_{in} - Cd_{out}) * 100/Cd_{out}$

Fig. 8 shows that, next to liquid/liquid interaction and CaF_2 precipitation, part of initial cadmium in the effluent is moved out. Consequently and in accordance to the matter conservation law, the lost cadmium is necessarily retained with calcium fluoride precipitate. As established, retention rate varies depending on pH, in case of Jeffara aquifer water, the

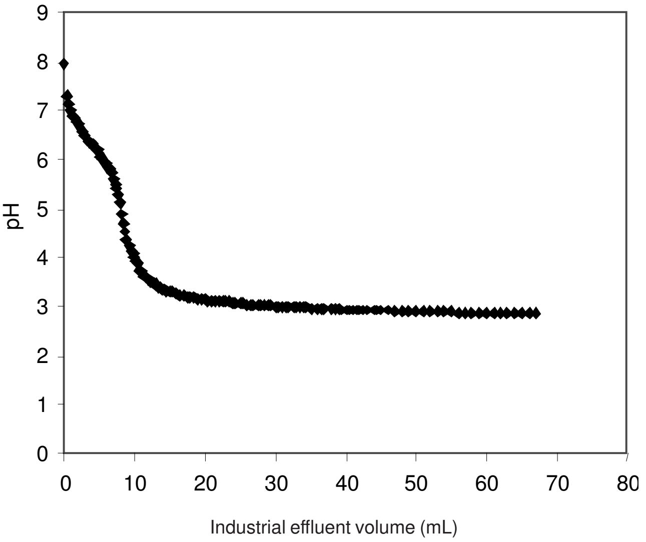

Fig. 5. Variation of the Jeffara water pH depending on the effluent added volume

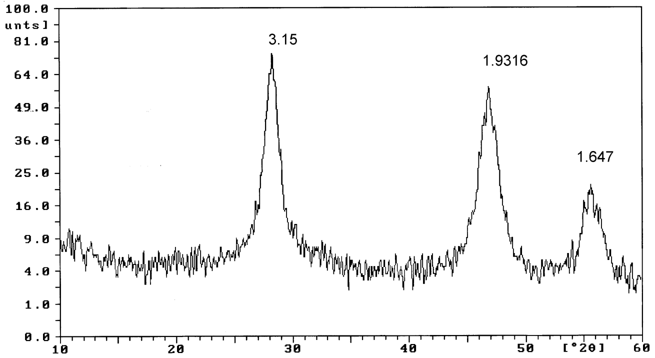

Fig. 6. Diffractogramme of the precipitate (effluent/Jeffara water)

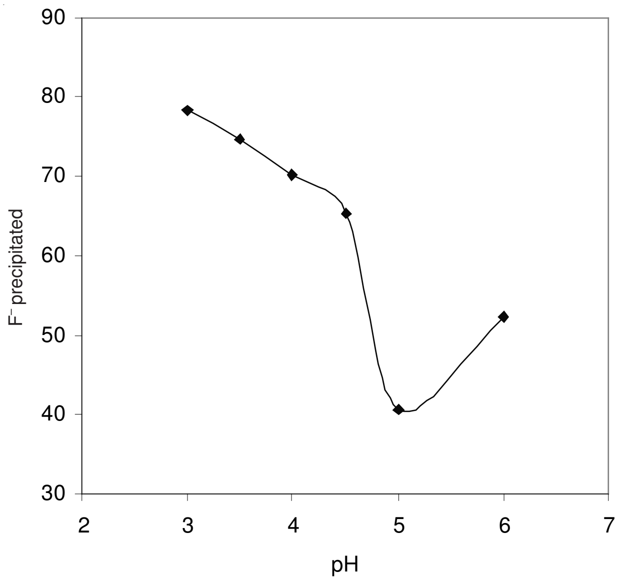

Fig. 7. Change in % F^- precipitated from Jeffara water as a function of pH

highest retention rate (64 %) lays in pH range 5-6. This result suggests that newly formed calcium fluoride is a good material capable to maintain Cd^{2+} ion (adsorption). Such phenomenon may form a barrier against the diffusion of cadmium in the environment.

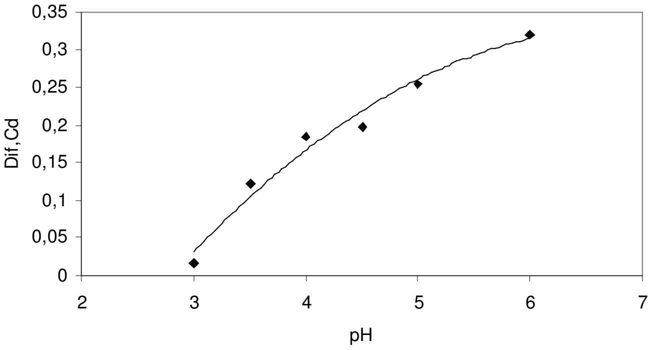

Fig. 8. Changes in Dif. Cd in Jeffara water as a function of pH

In order to better appreciate cadmium and fluoride decrease in the industrial effluent next to industrial effluent/soil interaction, the above liquid/liquid approach is applied to solid/liquid recorded results. Indeed F^- concentration variation in the effluent as a result of the interaction with different soils is illustrated in Fig. 9. There is a decrease in F^- concentration in the solution associated to the increase in carbonate rate in the soil. This observation is in agreement with the previous results concerning the interaction of industrial effluent with Jeffara aquifer water. It is very likely that this is linked to the formation of CaF_2 during the contact of the two involved phases.

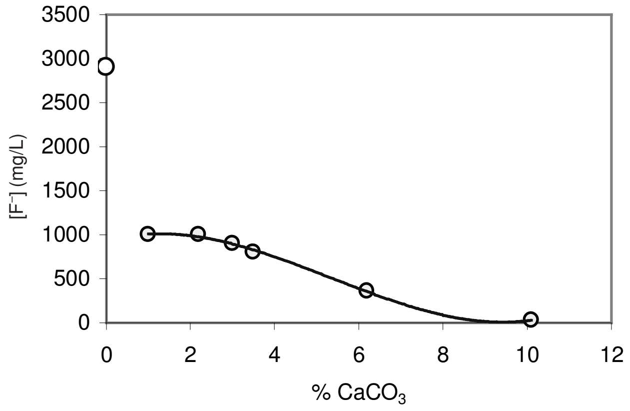

Fig. 9. $[F^-]$ variations in the effluent depending on the $CaCO_3$ content in the soil

An examination of Fig. 10 confirms this hypothesis, indeed the lowest Cd content is recorded for the interaction of industrial effluent with the more rich $CaCO_3$ (10%) soil.

Considering the previous results, it is permissible to accept the formation of CaF_2, following the neutralization of the industrial effluent further its contact with carbonates included in soil. The formation of this compound (CaF_2) explains easily the recorded decrease in Ca^{2+} and F^- as well as in heavy metals such as Cd^{2+}.

Conclusion

This work permits to study the interaction between an industrial effluent with two components of the natural environment: Jeffara aquifer water and ground sediments from Gabes area. Next to liquid/liquid contact, the formation of a precipitate which quantity varies depending on pH of the medium is observed. Chemical analysis and X-ray diffraction

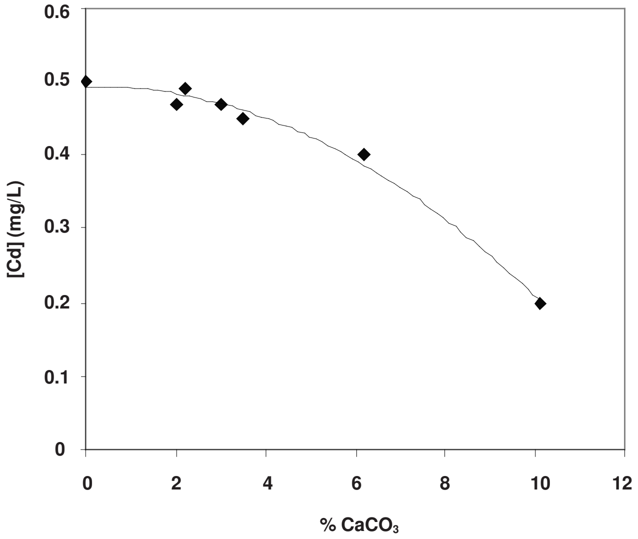

Fig. 10. Trends in [Cd] in the industrial effluent according to [$CaCO_3$] in the soil

of the precipitated solid, prove that it corresponds to calcium fluoride (CaF_2). Chemical analyses of filtrates that form during the studied reactions confirm that cadmium tends to disappearance from the liquid phases. This observation leads us to calculate matter balances, to conclude that Cd^{2+} ion can only be adsorbed by precipitated solid phase or co-precipitated with it. The retention rate of this component depends particularly on pH and nature of the solution that comes into contact with the industrial effluent. These results are very revealing, indeed solid phase that forms may constitute a barrier against the diffusion of F^- and Cd^{2+} in the receiving environment. Following solid/liquid contact, F^- as well as Cd^{2+} contents decreases are observed. For explaining such results, similarity with liquid/liquid was established and consequently CaF_2 formation and Cd^{2+} adsorption are admitted. Finally it is expected that the effect of the industrial effluent on natural environment will be horizontally restricted and with no vertical expansion due to pH neutralization and ions species retention.

REFERENCES

1. A.B. Chrifa, Thèse Complémentaire, Pollution et Dépollution par les phosphates, Faculté des sciences de Tunis, Tunis, Tunisa (2002).
2. M.P. Cescas and P.D. Agron, Projet PRICAT, Thème du Phosphogypse (1999).
3. S. Mangin, Généralités In LCPC, Bulletin de liaison des Laboratoires des Ponts et Chaussées, numéro spécial VII, Le phosphogypse; Utilisation d'un Sous Produit Industriel en Technique routière, Chapitre I, pp. 7-13 (1978).
4. E.J. Reardon and Y. Wang, *Environ. Sci. Technol*., **34**, 3247 (2000).
5. L. D'Avout d'Auersteadt, *Nuisances Environ*., **51**, 39 (1976).
6. X.D. Zhou and S.C. Kot, *J. Environ. Hydrol*., **3**, 367 (1995).
7. B. Hajem, H. Hamzaoui and A. M'nif, *Desalination*, **206**, 154 (2007).
8. Y. Wang and E.J. Reardon, *Appl. Geochem.*, **16**, 531 (2001).