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# Environmental technologies based on geochemical processes*

R.D. Schuiling
*Geochemistry Group, Institute of Earth Sciences, University of Utrecht, P.O. Box 80021, 3508 TA Utrecht, The Netherlands*

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**Abstract**

The accumulation of potentially harmful substances in our environment bears a close similarity to ore-forming processes; this is particularly evident in the case of inorganic pollutants. A look at the ways in which Nature minimizes the impact of high concentrations of toxic substances on the environment can provide inspiration for environmentally sound sanitation techniques. At variance with official environmental policies in the Netherlands, but in line with the basic aims of environmental science, it is often better to leave contaminated sites untouched, than to mobilize toxic substances during sanitation, or pretend to isolate them forever from contact with the biosphere.

## Introduction

When Society first became confronted with the consequences of our industrial and agricultural activities, and not in the least with the waste production of an increasing population with increasingly wasteful habits, most people considered this to be a unique phenomenon. It was hardly ever realized that Nature itself produces, and has produced in the geologic past, large concentrations of toxic substances. In most instances it has been able to cope reasonably well with the environmental consequences. I am talking, of course, of ore deposits, of oil and gas accumulations, and of the production of acids by volcanoes and/or weathering. Whereas the earth scientist is avidly searching for ore deposits, man-made 'ore-deposits' are considered to be a threat to the biosphere, and particularly to the health of mankind. Although I have the suspicion that the dangers are often overestimated, in a number of cases contamination of the environment can be harmful. My thesis is, that the knowledge we possess about geochemical processes and geochemical cycles permits us to devise technologies that are compatible with Nature, and that effectively eliminate possibly harmful effects arising from the accumulation of pollutants. This knowledge also permits us to predict how a contamination will behave under certain imposed conditions. This is particularly true when we are dealing with sub-

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stances that already occur naturally, in contrast to a large number of organic substances that were first synthetized by man.

The larger part of this lecture will deal with examples of technologies based on geochemical processes, that are investigated by the geochemistry group in Utrecht. Before presenting these examples, however, I first want to discuss the analogy between possible sanitation technologies and natural processes (Schuiling & Zuurdeeg, 1988).

**Environmental options**

One possible way to fight pollution is to convert the toxic substance into a small, but highly concentrated volume, which can either be deposited in a controlled site, or even better, be recycled (i.e. be treated as an ore). The evident analogy in nature are most ore-forming processes, which have in common that by some geochemical process an element or compound from a large, low-grade environment is concentrated into a small, high-grade deposit.

The opposite approach can also be used, namely the dilution of the pollutant to such low concentrations (and concomitantly large volumes), that the pollutant ceases to be toxic, c.q. reaches a concentration below the legally admissible threshold. It should be noted in passing that the concentrations below which no harmful effects are detected and the legally admitted threshold values bear little if any relation to each other. The analogy with nature is obvious; no ore deposit is a permanent feature in nature, and at a given moment it will suffer weathering, erosion and dispersion.

The most popular approach to environmental problems nowadays in the Netherlands is isolation. By making an impermeable base under our waste deposit, and an impermeable cover over it, the pollutant is isolated from the biosphere, and the problem is apparently solved. If isolation would indeed be a permanent solution, it would forever claim part of our living space. The idea, however, that any kind of isolation can be permanent is obviously wrong from the viewpoint of an earth scientist. At some unknown moment in the future, in some inpredictable way such a deposit will start to leak; every isolated waste repository is a time bomb for future generations. The only justifiable recourse to isolation is if the substance to be isolated disintegrates when left to itself (radioactive waste or degradable organic matter), or if isolation is a temporary measure until a proper sanitation technique has been developed. Isolation occurs many times in nature as well; impermeable cap rocks or clay formations can act as barriers, protecting underlying element concentrations from being mobilized.

The next possibility we wish to mention is immobilization; in this case the pollutant is immobilized by converting the substance into an insoluble compound (mineral), or by mixing it with an immobile material (concrete, glass). The problem, of course, is that such transformations change nothing in the concentration levels in which the contaminant is present, so the substance still falls in the dangerous category according to Dutch environmental regulations, notwithstanding the fact that it no longer constitutes an environmental hazard.

Immobilization is a very common and effective process in nature. As an example we will briefly describe the arsenic 'pollution' that was reported in 1987 in Baarloo. Very high levels of arsenic, up to 14 times the C-value (sites with concentrations above C-values must be cleaned up) were discovered at a new building site at Baarloo. Investigation by a team of Utrecht geochemists showed that the arsenic enrichment was due to the upwelling ('kwel') or ironbearing reduced groundwater. As it moves towards the surface, the iron in the groundwater is oxidized and precipitates as amorphous Fe(III)-hydroxides. The arsenic in the groundwater is quantitatively coprecipitated. If the iron content of the groundwater is e.g. 3 mg/liter, and the arsenic content 4 $\mu$g/liter, an iron precipitate with 30% iron will contain 400 ppm arsenic, i.e. 8 times above the threshold value for chemical waste. A major problem in contaminated sites is the possibility that children will ingest polluted soil. We have, therefore, carried out experiments on the mobilization of arsenic from the Baarloo soil in gastric juices. It was found that the arsenic is tightly bound, and that even after several hours in gastric

juices it will not become mobilized (Zuurdeeg et al., 1988). The Province of Limburg and the community of Baarloo have decided against sanitation of this site, at a saving of probably well over one million Dutch guilders.

Another example of immobilization concerns the fate of heavy metals in reduced underwater soils in the form of sulfides; as long as the conditions remain reducing, this is a very effective way of immobilizing a large number of heavy metals. The lesson to be learnt from this is that dredged sludges should be disposed of under water, in stagnant conditions.

**Environmental technologies**

Let us turn now to environmental technologies. A disadvantage of many natural processes, which could be used as a blueprint for environmental technologies is the fact that many of these processes proceed at slow rates. Once a natural process is identified as a promising solution to an environmental problem, measures must be taken to accelerate the process to make it technologically feasible.

*My first* example concerns the neutralisation of industrial waste acids (Schuiling et al., 1986), more in particular the sulfuric acid from titaniumdioxide plants. When an industrial acid becomes too diluted or too polluted, it must be discharged, neutralized or recycled. For various reasons the recycling of dilute, polluted sulfuric acid is not attractive, but neither is neutralization with limestone, because this produces large quantities of contaminated gypsum. By analogy with the natural process of weathering, we have devised a process in which olivine is used as the neutralizing agent. Olivine occurs abundantly in nature, it is the most weatherable of the common silicates, and the olivine process produces some attractive by-products. When the olivine is ground, and the process is run at temperatures of 70–100° C the process is essentially completed (i.e. 99% of the acid is neutralized) within a few hours. Moreover, the process is exothermic, thus after an initial heating the process sustains itself without energy consumption. Silica precipitates spontaneously, and we are capable of conditioning the polymerization and growth of the silica in such a way that a reasonably filterable product is obtained. After washing this is a good commercial grade of silica. The acid from the titaniumdioxide plants contains elevated amounts of vanadium and chromium. These are precipitated in our process into a small volume at pH around 4, under reducing conditions. After further neutralization the iron from the acid, originating from the acid itself as well as from the olivine, is oxidized and precipitated. We are able to precipitate the iron in the form of a crystalline iron oxide, which is fine-grained, but very easily filterable. Nickel can be selectively recovered from the olivine by using existing technology. Although the olivine process is elegant, effective and economically attractive, it has not yet found application, as the industry for which it was developed in the first place had to modify its production process so as to comply with environmental deadlines imposed by the Ministry of Transport and Public Works. The titaniumdioxide plant will shift to the chloride process, which requires synthetic or natural rutile as feed. As natural rutile is expensive and scarce, this means that synthetic rutile ('beneficiate') must be produced from ilmenite. As this involves often the use of sulfuric acid, the Dutch decision to shift to the chloride process boils down to the export of environmental problems to other countries.

Although the development of the process was made possible with the support of the Ministry of Housing, Physical Planning and Environment, as well as the industry concerned, the application of the process and its introduction as innovative environmental technology was made impossible by shortsighted Dutch environmental policy. Objections were also raised against the possible dumping of the final clean $MgSO_4$-solution at sea, although magnesium and sulfate are the second most abundant cation and anion in seawater. Sticking to senseless regulations with disregard for natural conditions seems to prevail over care for and a rational approach to the environment.

*My second* example has a curious beginning; in

1979 a cinema at the Nieuwedijk in Amsterdam burnt down. As the medieval origin of the town is located in this area, the Archeological Service of Amsterdam obtained permission to excavate the site during half a year, before a new building was erected. Next to rich finds of 13th century habitation, a large number of up to 1 cm sized brownish crystals were found. These found their way to my desk, and I determined them to be struvite (= $NH_4MgPO_4 \cdot 6H_2O$, Kars et al., 1980; Wevers et al., 1981). Obviously these crystals had grown in a place where the inhabitants of old Amsterdam dumped their offal, faeces and urine. Under anaerobic conditions this rich mix was mineralized. It is obvious that under the right conditions nature can eliminate the phosphate of organic waste streams by precipitation of struvite. Most phosphorus-bearing organic waste streams contain a stoechiometric excess of ammonia and potash (which can replace ammonia in struvite), but are lacking in magnesium. A second problem is the fact that their pH usually has values at which most of the phosphorus is present as $H_2PO_4^-$ or $HPO_4^{2-}$ ions, instead of $PO_4^{3-}$, which is required for the formation of struvite. By adding a slurry of MgO, both problems are overcome at the same time, according to the reaction

$$H_2PO_4^- + MgO \rightarrow Mg^{2+} + PO_4^{3-} + H_2O$$

Because the MgO is poorly soluble, it takes 1 to 2 hours before the reaction is complete; thanks to the sluggishness of the reaction, the struvite crystals grow to an appreciable size, settle rapidly and can easily be filtered and dewatered. The product constitutes a valuable slow-release fertilizer. We can make the process economically even more attractive by using ground magnesia bricks from steelworks (the magnesia linings must be replaced after a number of charges) instead of chemical grade MgO. The process has been tested on denitrified calf's dung (in which case a pure potassium struvite precipitates), and on the organic waste streams of potato and milk industries. In all cases high removal rates of phosphate were achieved, up to 99%. After we had developed the process, a literature survey showed that a somewhat comparable process had already been developed in Italy (Liberti et al., 1984) for the treatment of urban waste waters; in their case a preconcentration of phosphate on anion columns is necessary in view of the low phosphate concentrations. In my opinion the struvite process is at an advantage in the treatment of organic waste streams with high phosphate loadings. For low phosphate loadings, an attractive method has been developed by the Engineering Bureau DHV. The prototype of their pellet reactor will soon be tested. The struvite process as well as the pellet reactor are both superior to commonly used techniques for phosphate removal by the addition of aluminium or iron salts, which result in the production of phosphate-rich waste material.

*My third* example concerns the treatment of fluorine-rich drinking waters. In many semi-arid countries the groundwater contains excessive amounts of fluorine, leading to fluorosis, a crippling bone disease. In such climates the groundwaters evolve by evaporation and evapotranspiration, and in all cases the first mineral to precipitate is calcite. Depending on the ratio of calcium to alkalinity, the waters will subsequently follow different lines of evolution (Vergouwen, 1981). If calcium is in excess of alkalinity, the waters will become hard waters of the gypsum type, in the opposite case the waters will follow a trend towards soft, soda-type waters. Concentrations of fluorine in most natural waters are limited by the presence of calcium, because fluorite ($CaF_2$) has a low solubility. For that reason fluorine-rich waters are usually confined to waters of the soda-type, from which the calcium has virtually been eliminated by precipitation of calcite (Schuiling et al., 1988, p. IX-19). Technically, the elimination of fluorine from water poses no problem, but most of the proposed solutions require a certain level of technological development. The rural populations in areas affected by fluorosis generally lack technical skills, and we are aiming, therefore, at a method which requires no daily maintenance nor technical skill. The basis of our defluoridation method is the addition of calcium to the waters by passing them over filterbeds of gypsum sand. The fluorine is then removed according to the simple reaction

$$CaSO_4 \cdot 2H_2O + 2F^- \rightarrow CaF_2 + SO_4^{2-} + 2H_2O$$
(gypsum) (fluorite)

In laboratory experiments it was found that gypsum dissolution, even from fairly coarse-grained material is not rate-limiting. The precipitation of fluorite presents some problems in the absence of fluorite seeds. The gypsum filter material is mixed, therefore, with fluorite seed crystals although it seems illogical to achieve defluoridation by the addition of fluorine-bearing minerals. Experiments with pure water, to which fluorine was added, as well as with real groundwaters from a fluorosis-affected area in India showed that the fluorine content can be reduced to around 2 ppm, which is only slightly in excess of the WHO-norm for drinking waters (= 1.5 ppm F). Even so, it is expected that people drinking this defluoridated water will not show symptoms of fluorosis, or, in the worst case, will only have a slight mottling of the teeth, the mildest symptom of dental fluorosis. The defluoridation research is supported by the Ministry of Development Cooperation of the Netherlands, and is carried out in collaboration with the Applied Geochemistry Project of the Osmania University in Hyderabad under Dr. K.S.P. Rao. The method can be applied at individual wells in rural areas, and the raw materials required (gypsum and fluorite) are cheap and often locally available.

## Conclusions

I have given some examples how known geochemical processes can be modified and applied to solve environmental problems; by adopting such an approach we can be sure that no unforeseen complications will arise, as the process and the products are compatible with Nature. In support of this approach we may say that such processes have been tested over billions of years, and found to be effective to control high concentrations of harmful substances.

## References

Kars, H., Wevers, J.M.A.R. & Schuiling, R.D. 1980 Struvite, a mineralogical curiosity from an archeological site – Berichten Rijksdienst Oudheidkundig Bodemonderzoek (ROB) 30: 423–426.

Liberti, L., Boari, G. & Passino, R. 1984 Method for removing and recovering nutrients from wastewater – Bull. Eur. Patent Off. 84/30.

Schuiling, R.D., van Herk, J. & Pietersen, H.S. 1986 A potential process for the neutralisation of industrial waste acids by reaction with olivine – Geol. Mijnbouw 65: 243–246.

Schuiling, R.D., Andriessen, P.A.M., Kreulen, R., Poorter, R.P.E., de Smeth, J.B., Vergouwen, A.A., Vriend, S.P., Zuurdeeg, B.W. & Hoogewerff, J.A. 1988 Introduction to Geochemistry. 5th ed. – Dept. Geochem., Univ. Utrecht: 305 pp.

Schuiling, R.D. & Zuurdeeg, B.W. 1988 Natuurlijke processen als oplossing voor milieuproblemen – Milieu 2: 46–50.

Vergouwen, A.A. 1981 Salt minerals and waters from soils in Konya and Kenya – PhD thesis, Wageningen: 140 pp.

Wevers, J.M.A.R., Kars, H. & Schuiling, R.D. 1981 A struvite occurrence in Amsterdam – Bull. Miner. 104: 686–689.

Zuurdeeg, B.W., Coenegracht, Y.M.A. & Vriend, S.P. 1988 Evaluatie gezondheidsrisiko arseenverontreiniging Baarloo – Rapt. Gemeente Maasbree III/BWMT: 50 pp.