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ACCIDENTAL WATER POLLUTION CAUSED BY 16,000 BOTTLES OF "SAUTERNES"

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ABSTRACT

During the winter of 1975, 12 m^3 of wine accidently polluted the water well of a "château" in the Sauternes région.

After discussing the accident, we will study the contamination of the water and our measures to purify the well.

INTRODUCTION

We had previously experienced a successful decontamination of an alluvial water bed almost without stopping the supply of water to a population of 10,000 people (1).

As we were facing an apparently trivial pollution we expected to overcome it rapidly. After 3 years the problem remains unsolved, we therefore describe our difficulties : first the accident, then the pollution and the means implemented to resorb it as well as the causes of our relative failure.

THE ACCIDENT

It took place in a "château" of the Bordeaux region where a great Sauternes wine is produced. Formerly, before bottling the white wine the barrels were put outside in winter in order to precipitate deposits commonly called "wine stone".

On February 14th 1977, experimentally the cryogenic device of a 5 CV cooler was inserted in a 25 m^3 buried concrete tank full of wine and located in a "chai" (wine cellar).

The evolution of the temperature of the wine was checked so as to remain at -5°C during 5 days. After a 12 day period the tank leaked and 11.673 m^3 of wine (the equivalent of 16,000 bottles) were poured into the soil.

HYDROGEOLOGY OVERVIEW

The "château" was supplied by a single well meeting its needs. The water came from precipitations on a small basin the nearest part of which is the "château" ground and can be considered as a protection area. The aquiferous soils are composed of fluviatile alluvions with aeolian deposits. On the surface one observed coarse gravels, sands and silts where there are probably lenticular levels rich in colloids ; ferric compounds are abundant.

When the accident occured the water level in the well was located at over 6 meters under the ground which is about 4.30 m below the tank bottom. Thus the tank was in the so-called non saturated zone.

TANK DEGRADATION

The tank leak can be explained by fluid mechanic considerations. In these soils with vertical contrasted permeabilities and according to Darcy's law the horizontal transfer speeds (V_H) are much higher than the vertical transfer speeds V_V.

Assuming that the bi-layers have the same thickness this yield the following speed ratios as a function of permeability ratios.

Permeability ratios	10.0	100.0	1000.0
Speed ratios	3.0	22.5	250.5

There is no reason why in the non-saturated zone these ratios (gas-fluids) shoud be very different. Transfers with a dominating horizontal component become preferential in sheet soils, since for gases gravitation plays no part.

Considering that soil humidity is near the saturating vapor tension, we see that when temperature goes from 12°C to 0°C the absolute humidity falls from 11.0 gm^{-3} to 4.85 gm^{-3}. Soil cooling produces 6.15 gm^{-3} of water condensation. According to the "cold wall" principle in the vapor phase, transfer, condensation and water solidification take place of course with calorie absorption. Adding this to the soil humidity (liquid) which is very high in winter in our climates we understand that very soon the medium becomes almost liquid saturated.

From the walls, a preferential segregation of the 3 water phases occured, followed by "pipkrake" formation. The ice thus formed is not theoretically isotropic, the pressure sometimes prevents the water from icing up. Liquid water cells caught in ice must have been formed, the water was thus immobilized. As the process from liquid to solid water causes an expansion and as the solid medium has a limited compressibility a rise in pressure took place.

In a solid medium and on this scale convection is low and conduction limited, the ice formed orthogonally to the thermal flow insulates better than water ; an increasing energy built up in a thermodynamically more and more closed medium ; hence a more and more efficient "hydraulic jack" was constituted. The usable energy (we don't know with precision the efficiency) was considerable as it was equivalent to 1250 kg T.N.T. combustion.

The tank bottom could not withstand it, it broke up in a star shape. The loss of the wine which, to leak away had to melt the ice, can be explained because being very far from its freezing point (-12°C) made a cryogenic mixture (Raoult's law) with the water.

POLLUTION

Althought the distance separating the tank from the well dit not exceed 17 m it took a long time to associate the well pollution with the wine loss. All other possible causes were investigated.

The 11.7 m^3 of wine must have contained roughly 1.5 t of organic matters (normally nicely biodegradable) containing :

Alcohol	1310 kg
Tartric acid	58.5 kg
Glycerol	176 kg
Polyphenol	5,85 kg
Iron	**11,7 kg**
Copper	4.1 kg
Sulphured compounds	

In Autumn 1977 during one of our visits we noticed that the well water had an intolerable taste and smell. On contact with the air it yielded saprophytic colonies of mucilages aggregation in "flocks" and exhibited large amounts of ferric iron. Except for the organoleptic characteristics and the presence of iron, the classical legal analysis met the standards for drinking water. The owner of the "château" claimed that the well flow rate had much decreased.

Pollution had been attracted towards the well, the wine decomposition took place in a reducting medium, the soil iron had been solubilized and the presence of sulphure compounds induced thiols. To eliminate pollution only required the biodegradation acceleration by supplying oxygen and extraction residues. In short, the water bed transfer increase together with a level decrease (i.e. pumping) were necessary.

DECONTAMINATION ATTEMPTS :

After placing a water level and a "Pitot" recorders we determined the aquifer characteristics. The time required to reach the tank level with the depression was estimated at 12h. From the supposed water bed flow and from the contaminated areas estimate, previsionnal calculations indicated that a pumping time of some 3 months would be necessary.

Four pumpings of a cumulated duration of 150 days were carried out to extract 5000 m^3. The water pumped out was rejected 200 m downstream and formed a pond which made the entrance to the "château" difficult.

We also thoughtthat during break periods a natural decontamination would occur.

A few days after each pumping began, the well surface becomes iridescent (organic matter in quasi-monomolecular film), this would disappear later on. Pollution seemed to decrease with however a tendency to stabilize itself. But on the next pumping we found a water which had apparently recovered part of its pollution.

In November 1980 we undertook at a very low flow rate (10 m^3 per day) a test which is still going on. We checked almost daily, over a month and weekly afterwards, the major physico-chemical elements of the pumped water (with Hach Drel2 portable test equip). The main results are presented table 1 and we notice the following facts :

- the extracted iron quantity exceeds that contained in the wine.
- a quantity of nitrates and nitrites was pumped out whereas the wine contains very few nitrogen compounds.
- carbonic anhydride contents indicate a slight gas removal of the water at atmospheric pressure. It proves that epuration takes place with a hig air percentage in the gaseous phase.
- chloride concentrations are relatively stable.
- sulphate and bicarbonate contents are not significant even though a mineralisation seemed to occur at the beginin of the pollution.
- the water contained in bottles at 20°C evolves quickly ; after 1 to 3 days a flaky deposit appears which little by little becomes a very small black aggregate apparently constituted of carbon possibly associated with non soluble metal sulphides.
- the concentrations of elements associated with the contamination undergo fluctuations much higher than possible analytic errors as if elution took place in successive waves.

There are still very few nitrites and the ratio nitrates over nitrites although variables seems to vary more slowly than the contents themselves.

The Flyght pump equipment Bibo 1 located in the well provides a flow all the more powerful as the level is higher. We thus expected a pseudo-stabilisation which was never achieved.

The influence of the rain alone is not sufficient to explain these anomalies ; we felt that self epuration processes occur with different velocities dependent on one another. It is as if the soil behaves with the wine like a huge chromatographic column. The soil and the preexisting organic matter from beneath the tank absorbed preferentially certain wine compounds. Micro-organisms attacked pollution in a highly reducing medium (glycerol) ; decomposition products consumed by other micro-organisms provided soluble compounds which went to the well ; there under new micro-organisms they generated mucilages and aggregates which we sometimes pumped out and which must clog the soils. That is why the oxygen from the water bed reaches them with more and more difficulty.

The energy generated which is easily consumable allows furthermore the attack on previously fossilized organic matter.

We pump out a water mixture from a medium where because of the "blocking" (acting as a protective layer) and because of the slowness of certain processes it is not possible to activate decontamination.

The water bed regeneration seems to be tributary of the slowiest phenomenon ; the low soil temperature makes by the wa, the work of the micro-organisms relatively slow (2).

CONCLUSIONS

From the accident described and the subsequent observations we can draw the following conclusions :

- Under the influence of a temperature gradient the transfers of water in vapor phase can be very important.
- The legal chemical analyses are not representative of certain pollutions.
- Soils behave like a huge chromatographic column where micro-organism colonies protect themselves in waterproofing locally the aquifer.

From threshold effects the slowiest phenomenon imposes its speed on the wole epuration process.

- It can be dangerous to enclose in homothermic medium beyond the reach of plant roots organic matters with a high energy power.
- Before generalishing more or less epurated effluent injections in soils, it would thus be reasonable to study methodically the various self-epuration processes as a function of pollutants on one hand and the nature and dimension of soil pores on the other hand (3).

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Date	pH (13°C)	TH (Ca)°F	TH (Mg)°F	CO_2(mg ℓ^{-1}	SO_4^{--}(mg ℓ^{-1})	Cl^-(mg ℓ^{-1}	NO_3^-(mg ℓ^{-1})	NO_2^-(mg ℓ^{-1})	NO_3^-/NO_2^-	Fe(mg ℓ^{-1})	Mn(mg ℓ^{-1})	Fe/Mn	Cu(mg ℓ^{-1})
25-05-77	6.65	27.4	3.6		34	35.5	0	0		1.0			0.16
08-02-80	6.74	24	2.5		40	25	8.8	0.09	98	2.4	0.8	3.0	0.12
11-02-80	6.55	19	3.0	124			12.3	0.092	134	3.0	0.45	6.6	
20-02-80	6.48	19	3.5	116	52	22.5	11.4	0.042	271	2.1	0.5	4.2	0.19
29-02-80	6.43	18	3.0	100	40	35.5	17.6	0.085	207	2.35	0.30	7.3	
21-03-80	6.46	18	2.2	76	60	25.0	16.7	0.09	186	1.00	0.35	2.9	
25-04-80	6.46	22	2.0	96		30.0	18.5	0.09	205	0.23			0.03
20-11-80		18	3.0	132	58		4	0.03	133	0.75			0.10
21-11-80		17	4.0	112	50	25.0	3.9			0.85	0.30	2.8	0.15
24-11-80	6.49	19	4.0	190	50	25.0	4.8	0.03	160	0.55	0.24	2.3	0.25
25-11-80	6.40	19	3.0	116	50	25.0	2.8	0.08	35	0.53	0.20	2.7	0.02
27-11-80	6.60	18	4.0	112	52	25.0	3.5	0.03	116	0.47	0.10	4.7	0.08
01-12-80	6.60	18	4.0	84	58	30.0	4.1	0.04	102	1.05	0.10	10.5	0.02
04-12-80		18	4.0	112	50	25.0	3.3	0.03	110	0.90	0.30	3.0	0.10
08-12-80	6.58	18	5.0	112	51	25.0	3.8	0.03	127	0.90			0.15
12-12-80	6.45	19	6.0	80	46	25.0	3.3	0.024	137	0.80	0.10	8.0	0.08
15-12-80	6.55	19	5.0	92	50	25.0	3.8	0.03	127	0.60	0.20	3.0	0.09
18-12-80	6.58	19	4.0	96	50	25.0	4.0	0.02	200	0.80	0.30	2.7	0.14
02-01-81	6.41	18	5.0	116	47	25.0	4.0	0.03	133	0.53	0.20	2.7	
12-01-81	6.48	19	5.0	96	47	25.0	3.3	0.03	110	0.32	0.20	1.6	0.08

Table 1 : Main Analysis