Cyanide accident

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Lučební závody Draslovka a.s. Kolín (Draslovka Chemical Plants in Kolín)

Established in 1906.

Located in the periphery of Kolín Town, forming part of a large industrial zone.

The main business line consists in chemical production, production of hydrogen cyanide and other cyanic chemical products.

Furthermore, production of poisons and caustic products, storage and handling of chemical substances and products.

Lučební závody Draslovka a.s. Kolín

Based on the operator's notification pursuant to the Serious Accidents Prevention Act, the object has been included in group B.

17. –18.5.2005 - Inspection pursuant to the Serious Accidents Prevention Act

12.7.2005 - Safety report approval,
Effective from 1.8.2005

9.1.2006 - Escape of waste water with high cyanides content into the Elbe River

→ Serious accident

Cyanide Accidents in General

Causes of cyanides escapes in ground water have included technical and especially technological-operational failures. Other circumstances are moreover related specifically to cyanides:

- Failure to manage the disposal process, especially surge inflows of cyanide concentrates.
- Application of unqualified and/or quite improper analytical methods to check the deactivation effect.
- Failure of the waste water treatment plants attendance personnel and/or lack of knowledge of such personnel or failure to observe
- the proper detoxication procedure.
- Low level of the operator's knowledge on possibilities of emergency cyanides escapes outside of the premises, its functional failure etc.

A combination of multiple causes is usually present in cyanides escapes in ground water.

Course of the Accident in Jan 2006 (1)

- 10.1.2006 – Isolated occurrence of fish dying in Elbe River – Kolín; oxygen deficit was wrongly assessed as the cause
- 12.1.2006 – Mass dying of fish in the Elbe River – Nymburk profile and occurrence of blue colouring of ground water; presence of cyanides was found upon analysis (0.4 mg/L CN_{total} and 0.038 mg/L CN_{tox}).
- 13.1.2006 – CEI's investigation with the single possible originator of cyanide contamination – Draslovka Kolín; traces of waste water overflow into the rainfall drainage inlet were found.

Course of the Accident in Jan 2006 (2)

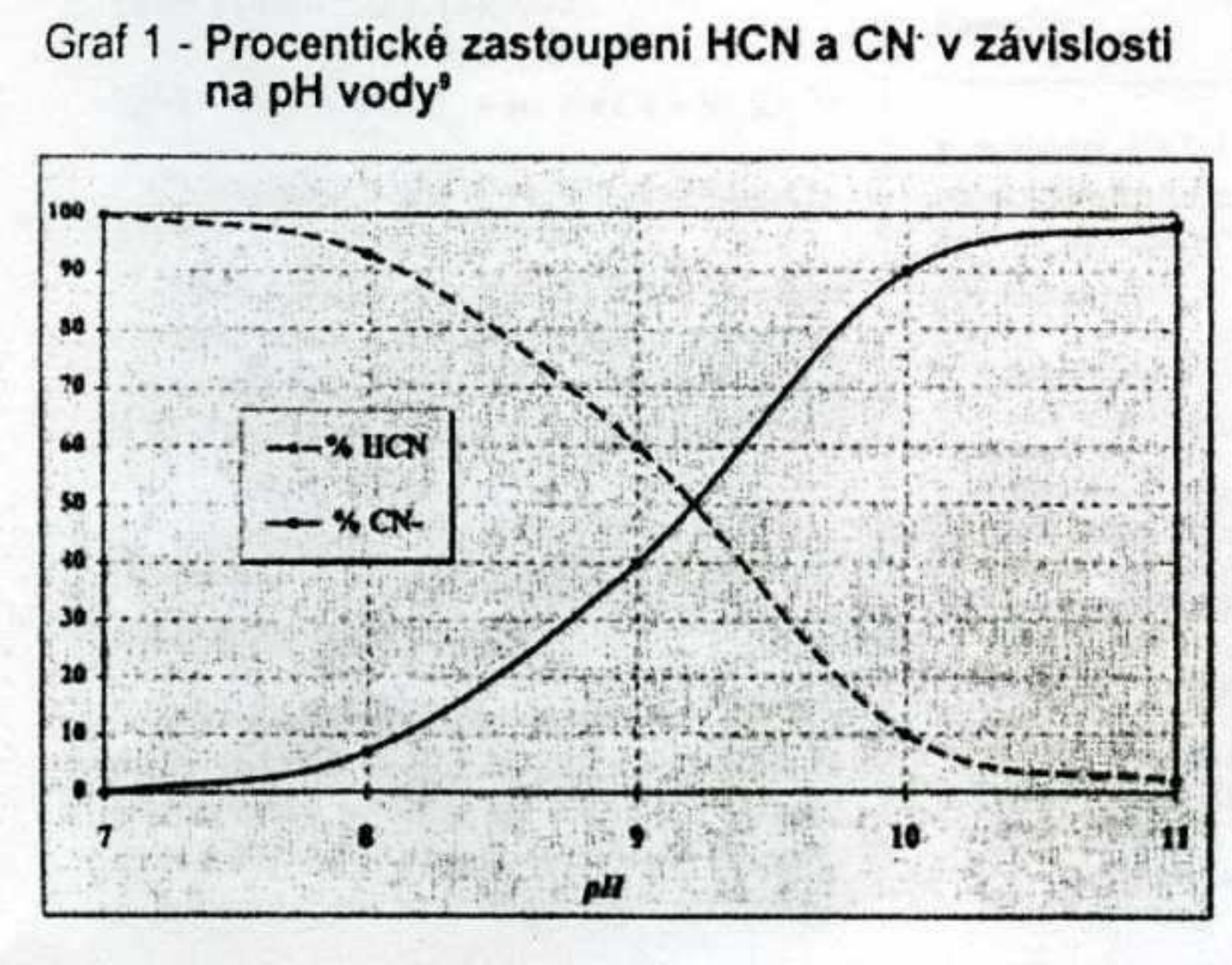
- 13.-21.1.2006 – Ground water quality monitoring in Elbe River to determine CN_{total} and CN_{tox} indicators provided by Povodí Labe (Elbe River Basin Administration). Check of cyanide contamination in the borderline profile with the Federal Republic of Germany, Elbe River – Schmilka, was provided by the German part during 18. – 23.1.2006.
- 16.1.2006 – CEI's investigation at Draslovka Kolín, a.s. upon which the cause of cyanides escape was determined to be the waste water overflow into rainfall drainage.
- 16.1. – 31.3.2006 – Commissional investigation of the accident causes and extent; expert opinions were elaborated etc.

January 16, 2006

Essential Data on Cyanides Behaviour in Ground Water (1)

- Cyanides occur in the form of simple or complex compounds in water. The first form is represented by the CN^- anion and undissociated HCN (weak acid with the dissociation constant 10-9) – See Graph 1.

Graph 1 – Percentage representation of HCN and CN^- in dependence on pH of the water



Essential Data on Cyanides Behaviour in Ground Water (2)

- Cyanide complexes with metals show various stability levels (those with Fe show the greatest stability) while CN^- ions are the product of their dissociation – See Table 1.

Complex compound type	Dissociation coeficient	Free cyanide amount in mg/L, corresponding to the initial concentration of the given complex compound		
		10 mg/L	100 mg/L	1000 mg/L
/ $Hg(CN)_4$ /	$4 \cdot 10^{-42}$	0, 00003	0, 000045	0, 00007
/ $Ag(CN)_2$ /	$1 \cdot 10^{-21}$	0, 0002	0, 0004	0, 0009
/ $Fe(CN)_6$ / $^{4-}$	$1 \cdot 10^{-42}$	0, 061	0, 085	0, 117
/ $Fe(CN)_6$ / $^{3-}$	$1 \cdot 10^{-36}$	0, 058	0, 081	0, 110
/ $Ni(CN)_4$ /	$1 \cdot 10^{-22}$	0, 215	0, 340	0, 54
/ $Cu(CN)_4$ /	$1 \cdot 10^{-22}$	0, 215	0, 340	0, 54
/ $Zn(CN)_4$ /	$1,3 \cdot 10^{-17}$	2,26	3, 59	5, 68
/ $Cd(CN)_4$ /	$1,4 \cdot 10^{-17}$	2,30	3, 64	5, 77

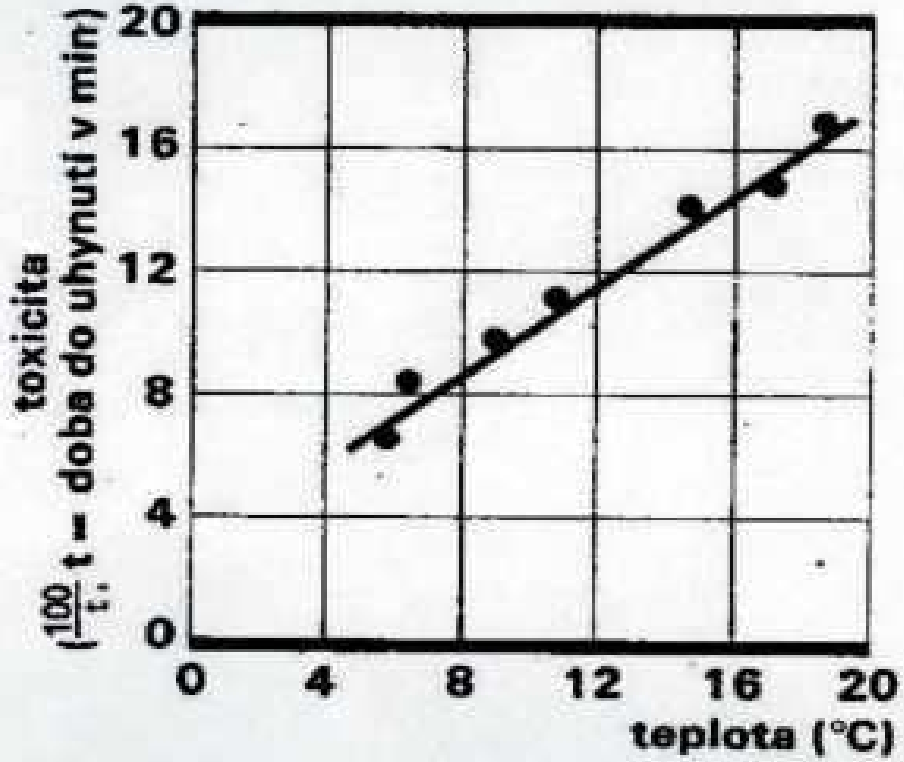
Essential Data on Cyanides Behaviour in Ground Water (3)

- Cyanides are highly toxic for fish.
- Safe concentration is given in the range of 0,003-0,005 mg/L; dying of fish occurs in the concentration range from 0.05 m/L. The toxic effects depend on the temperature, pH and oxygen content.

Toxicity dependence on temperatur

Axis y : Toxicity Time to death in min

Axis x : Temperature



1. Závislost toxicity na teplotě.

Essential Data on Cyanides Behaviour in Ground Water (4)

- Degradation of cyanides in ground water is given by numerous processes. Simple cyanides are not stable in water and the product of their dissociation – hydrogen cyanide – is volatile and its draught removal is one of the processes which take part in decreasing the amount of cyanides in ground water.

$$\log \frac{Ct}{Co} = k.t$$

Co – Initial cyanides concentration

Ct – Cyanides concentration at the time t

T – Time

K – Reaction rate constant (0.02 hr-1)

Origin and Cause of the Accident (1a)

- Draslovka Chemical Plants in Kolín was the source of the cyanides escape. The plant is situated on the left bank of Elbe River (river km 195). At present, cyanide water of two types is produced at the plant:

  a) From cyanide and HCN production

  b) From organic syntheses in which cyanides are used

- The first type of waste water with the CN content 10-300 g/L is disposed of by stripping in acidic environment at first – subsequently, detoxication is performed by oxidation using calcium hypochlorite. Upon sludge sedimentation, waste water is discharged in the plant's drainage system.

Origin and Cause of the Accident (1b)

- The other type of waste water with CN content reaching hundreds of mg/L and containing other organic substances (COD_{Cr} up to 8000 mg/L) is disposed of by complexation using $Fe2^{+}$ compounds and subsequent alkalization.

- The technology is operated in the complete cycle (including sludge sedimentation in the so called detoxication pits (3pcs, 120 m^3 each); waste water is further pumped through the sand filter into the plant's drainage system. The detoxication pits are found in the open space; historically, it is an object which has been operated on a long-term basis, and to which waste water has been repumped about two times a year, too, at the times of shutting down HCN and NaCN production (representing highly concentrated water used to rinse parts of the production equipment stopped for maintenance work).

Origin and Cause of the Accident (2)

The emergency situation at the object occurred during the night from the 8th to the 9th of January, 2006; at this time, the outside temperature dropped as low as -15°C, when concentrates produced by cleaning the technological equipment had already flown into the detoxication pit. Cause of the escape was due to overflow of non-deactivated waste water under the following circumstances:

- Freezing up of the water level floats;
- Absence of attendance personnel including incomplete operating records;
- Failure of output laboratory check of waste water discharged in Elbe River.

Measures of the Operator

- Blank the rainfall drainage system inlet;
- Provide doubling of the signalling system of float-based level indicators;
- Increase the frequency of visual checks of filling the detoxication pits, including increased accuracy of the checks and discharging records;
- Increase the analyses frequency of waste water discharged from the plant's drainage system into Elbe River.

Measures Proposed to State Administration

- Eliminate the concentrated waste water flow from HCN and NaCN production to the detoxication pits.
- Improve the operational supervision and analytical checks of cyanide water disposal.
- Add further risks of detrimental substances escape, not yet registered, to the water management emergency plan.
- Establish safety retention elements at the outlet point from the plant for the purpose of an intervention in emergency situations.

Thank you for your attention