
JOSEF STEBER
WOLFGANG HATER

Ecological Assessment of Chemicals for Treating Cooling Water

Abridged version of a paper presented at the VGB Conference "Chemie im Kraftwerk" in Essen from 29th to 30th October, 1997

Chemicals for treating cooling water to prevent deposits and corrosion processes in cooling circuits are expected to meet high standards not only in regard to performance, but also in regard to environmental compatibility. This is because, in normal open circuits, part of the cooling water is continuously removed and replaced by fresh water. In closed-loop systems, too, the cooling water has to be changed at certain intervals. Another obvious reason why environmental compatibility must represent an equal element of the requirement profile for cooling water treatment chemicals is that, in general, the cooling water is directly introduced into the aquatic environment without any preliminary wastewater treatment. The ecological acceptance of chemicals for treating cooling water must therefore be assured.

1. BASIC PRINCIPLES OF ENVIRONMENTAL SAFETY ASSESSMENT

The environmental safety assessment of chemical products is based in principle on the ecological properties of the individual ingredients of the product. The crucial ingredient-specific parameters for ecological evaluation are degradation behavior and aquatic toxicity because these properties critically determine the environmental fate of the product ingredients and their potential effect on organisms [1]. In accordance with the concept of the environmental risk assessment of chemical compounds applied across the EU, a prediction of the concentration in the environment (predicted environmental concentration, PEC) and of the concentration below which there is no longer any ecotoxicological effect (predicted no-effect concentration, PNEC) can be made on the basis of the ingredient-specific ecological data. Safety factors and boundary conditions governing the use of the particular product, such as the usage figures, the wastewater situation and the size of the receiving water, have to be taken into consideration. Whenever the PEC is

lower than the PNEC, i.e. whenever the PEC/PNEC quotient is <1 , the chemical compound in question can be assumed to pose no risk to the environmental compartment under consideration, for example a surface water.

Before the specific ecological evaluation of the individual ingredients of chemicals for treating cooling water is discussed in detail, attention is again directed to the performance aspect of the product. The product should satisfy technical requirements in the long term despite economical dosage levels. This is also a necessary prerequisite for environmental compatibility because, despite such favorable ecological properties, inferior performance would lead to unnecessary additional water pollution through increased dosages. The ecological safety assessment in the narrower sense must also ensure that the use of the product does not pose any environmental risk, i.e. persistence in the environment and critical environmental properties, such as ecotoxicity, bioaccumulation and heavy-metal remobilization, can be ruled out.

2. ECOLOGICAL EVALUATION OF SELECTED COOLING WATER TREATMENT CHEMICALS

Data from our own studies and data available from the literature and databanks were used for the ecological evaluation of technically important ingredients of chemicals for treating cooling water. The subject of the evaluation were the two phosphonic acids used to stabilize hardness and for dispersion, namely hydroxyethane diphos-

phonic acid (HEDP) and phosphonobutane tricarboxylic acid (PBTC), polycarboxylic acids of the polyacrylic acid type with a molecular weight of 3000-4000 and the nonferrous metal inhibitors benzotriazole and tolyl triazole, a mixture of 4- and 5-methyl triazole.

Besides acute and long-term toxicity, heavy-metal remobilizing potential was additionally evaluated in the case of the phosphonates and polyacrylates (Table 1). With effect concentrations (EC_{50}) of >100 mg/l, these compounds show a low acute toxicity towards fish and small crustaceans (daphniae). The corresponding data for benzotriazole and tolyl triazole are slightly lower in some instances, i.e. indicate somewhat higher toxicity towards aquatic organisms, although the subchronic and chronic long-term toxicity results are of the same order as those of the phosphonates and polyacrylates. The long-term toxicity tests, which are more informative and hence ultimately more important for risk assessment, determine the highest concentration which has no observable effects in relation to a control, which is known as the no observed effect concentration (NOEC). Criteria in these particularly sensitive tests are, for example, cell multiplication in the case of algae or the number of young produced in the daphniae multigeneration test. As expected, the NOEC values are lower than the acute effect data, although it was found that, for all the compounds in question, these values are never below 10 mg/l and are often above 100 mg/l. NOEC values of this order may be regarded as noncritical because the water concentrations of individual chemical compounds are generally well below 1 mg/l.

Complexing agents and ion exchangers can release basically toxic heavy metals from water sediments. However, the study data for the phosphonic acids and polyacrylates show that problems are unlikely to occur at the expected concentrations of <1 mg/l.

	Phosphonic acids [mg/l]	Polyacrylic acid [mg/l]	Benzotriazole/tolyl triazole [mg/l]
Ecotoxicity			
Acute aquatic toxicity (fish, daphniae) EC ₅₀	>100	>100	10 - >100
Long-term toxicity (NOEC) fish	>100	>100	-
daphniae	10 - 100	10 - 100	10 - 100
algae	10 - 100	>100	10 - >100
Heavy metal remobilization	No effect ≤2	No effect ≤10	Not relevant

	Phosphonic acids	Polyacrylic acid	Benzotriazole/tolyl triazole
Biological degradability			
ready biodegradability (OECD 301 A-F)	No	No	No
inherent biodegradability	No	Yes (river water)	Yes (OECD 302 B)
Abiotic degradability	Photochemical degradation (Fe complex)	-	-
Bioaccumulation potential	No (BCF<100)	No (MW>700)	No (log Pow<3)

The environmental fate of chemical compounds depends to a large extent on their degradation properties. Biological degradation usually plays the most important role in ruling out persistence and hence the danger of a steady increase in concentration of these compounds in the environment. As desirable therefore as the ready biological degradability of chemical compounds may be, it is still a problem in connection with the technical requirements which chemicals for treating cooling water are expected to meet. Conditioning agents are of course supposed to prevent or at least not promote the growth of organisms

in the cooling circuit. It is only in this way that fungal contamination of the cooling tower timbers, microbial growth in the cooling tower, blockages in heat exchangers and microbially induced corrosion can be controlled. For this reason, the poor biodegradability of HEDP and PBTC and the very slow biodegradability of polycarboxylates and the triazole derivatives may be regarded as entirely desirable (Table 2).

On the other hand, however, extensive studies of phosphonic acids [2] have shown that they can definitely not be regarded as stable in the environment and that abiotic degradation mechanisms exist. In the case of HEDP and PBTC in particular, the iron complex predominantly formed

higher organisms—rule out the accumulation of these compounds in aquatic organisms. The absence of a bioaccumulation potential ensures that the ingredient concentrations in the environment also correspond to the maximum expected concentrations in the organism and that, there-

Table 3

Environmental risk assessment of chemicals for treating cooling water (according to EU-TGD)

	Phosphonic acids	Polyacrylic acid	Benzotriazole/tolyl triazole
Exposure analysis (realistic worst case) concentration in cooling water*	≤ 5 mg/l (HEPD) ≤ 12 mg/l (PBTC)	5 mg/l	0.2 – 1 mg/l
PEC _{water} (dilution 1:100)	0.05/0.12 mg/l	0.05 mg/l	0.01 mg/l
Effective evaluation lowest NOEC or EC ₅₀ safety factor according to TGD	10/18 mg/l 10	12 mg/l 10	32 mg/l 1000
PNEC _{water}	1.0/1.8 mg/l	1.2 mg/l	0.03 mg/l
Risk assessment PEC/PNEC	<1	<1	<1

* With continuous addition of the treatment chemicals

in waters is photochemically unstable so that persistence in the environment can be ruled out. Polyacrylates are also slowly biodegraded, as long-term degradation studies with adapted aquatic bacteria have shown [3]. Benzotriazole and tolyl triazole were also found to be biologically degradable in principle under the conditions of standard tests for determining “inherent biodegradability” (OECD 302 B), so that in their case, too, there is no danger of any long-term increase in environmental concentrations.

Another aspect of importance to the ecological safety profile is not a problem for the discussed phosphonic acids, polyacrylates and non-ferrous metal inhibitors, namely bioaccumulation behavior (Table 2). The experimental results obtained for phosphonic acids, the high molecular weight of the polyacrylates and the low octanol/water distribution coefficient (Pow) of benzotriazole and tolyl triazole—a measure of the solubility of a chemical compound in the fatty tissue of

fore, the active concentrations critical to aquatic organisms are not underestimated.

3. ENVIRONMENTAL RISK ASSESSMENT OF CHEMICALS FOR TREATING COOLING WATER

The positive ecological evaluation based on the properties of phosphonates, polycarboxylates and triazole derivatives can be further concretized using the above-mentioned environmental risk assessment method stipulated in the EU for systematic product characterization (Table 3). In accordance with the EU Technical Guidance Doc-

ument [4], the predicted environmental concentration (PEC) is determined in an exposure analysis under conservative "realistic worst case" conditions and compared with the PNEC (concentration which largely rules out ecotoxic effects in the environment) derived from ecotoxicological studies. The exposure analysis of all three groups of cooling water treatment chemicals is based on the concentrations used in cooling waters disregarding any degradation or elimination processes. The assumption of a dilution factor of 100 between the cooling water and the receiving water may also be regarded as conservative in the context of existing regulations governing the discharge of cooling waters into receiving waters. This exposure analysis results in PEC_{water} values which are below the 1 mg/l threshold by a factor of at least 10, i.e. are in the 10-100 g/l range.

The PNEC is determined by the EU evaluation method based on the lowest end point observed in ecotoxicological standard tests, i.e. the NOEC for long-term data or the EC_{50} for acute toxicity data. Since long-term data from laboratory studies have a higher predictive value for real environmental behavior than acute data, these experimental concentration values are provided with a variable evaluation factor, a safety factor, to take account of the uncertainties involved in extrapolating laboratory results to the real environment. Accordingly, the safety factor to be applied, for example, where at least three long-term data are present is only 10 whereas, in the presence of three acute toxicity data, it is 1000. Since there are no long-term toxicity data for three organism groups, such as fish, daphniae and algae, in the case of the triazole compounds, the acute data were used to determine the PNEC—an undoubtedly very conservative approach

because the existing data show (Table 1) that the effect concentrations in the acute and long-term toxicity tests do not differ greatly from one another. On the basis of this effect evaluation, the $PNEC_{\text{water}}$ values for the three groups of active compounds are in the range from 0.03 to 1.8 mg/l.

Comparison of the predicted concentrations determined under such realistic worst case conditions shows that the predicted environmental concentration (PEC) in the water is well below the predicted no effect concentration (PNEC) for all cooling water treatment chemicals, so that the compounds in question pose no environmental risk when used under the discussed conditions.

4. CONCLUSIONS

The properties and environmental risk assessment of HEDP, PBTC, polyacrylates, benzotriazole and tolyl triazole allow the substantiated conclusion that their use for treating cooling water is environmentally compatible and offers an advantageous combination of performance and environmental safety.

Literature

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Correspondence authors:

Dr. Josef Steber, Henkel KGaA, Düsseldorf
Dr. Wolfgang Hater, Henkel KGaA, Düsseldorf