

Euroalliages^a Research Project For Environmental Hazard Evaluation of Ferroalloys and Slags

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ABSTRACT

The reported study aimed at giving a practical example how to establish the aquatic hazard assessment for ferroalloys and slags using recognised, scientific techniques. The following materials were tested: 'High Carbon FeCr alloy', 'High Carbon FeCr slag', 'FeV alloy' and 'FeMo alloy'. The testing methodology involves performing, acute dissolution testing, according to the (draft) guideline for sparingly soluble metals and metal compounds¹, followed by the ecotoxicological evaluation of the solution rendered after dissolution testing. In this particular study, either acute fish tests (*Danio rerio*) or alga growth inhibition tests (*Raphidocelis subcapitata*), were applied. In addition, the highest dissolved element concentrations observed during dissolution testing were compared with ecotoxicity data as reported from literature. Full transformation - dissolution testing with the 'HCFeCr-alloy' and the 'HCFeCr-slag' did not result in significant dissolved element concentrations. For the 'FeV-alloy' and the 'FeMo-alloy' dissolution of vanadium (831 µg/l) and molybdenum (8.25 mg/l) respectively was observed during acute tests

at a loading of 100 mg l⁻¹. For all solutions, no adverse effects were observed after their ecotoxicological evaluations. This observation is in line with the prediction "no ecotoxicity" from the literature as dissolved concentrations for the different elements were all (well) below the lowest reported acute ecotoxicity data for standard species of fish, alga and the crustacean *Daphnia magna*.

INTRODUCTION

An alloy can be defined as a metallic material, homogeneous on a macroscopic scale, consisting of two or more elements so combined that they cannot be readily separated by mechanical means². From the perspective of hazard assessment, considering alloys as mixtures or, alternatively, as a unique group needing self-classification, is currently the subject of debate within Europe. Accepting alloys to be mixtures may result in accepting hazard assessment for alloys, based on ecotoxicity data available for its individual components³, a strategy that will be further referred to as the conventional classification method. It is recognised that the physical and chemical properties of alloys can strongly differ from those of its elementary

^a Comité de liaison des industries de ferro-alliages (M. Fiat, Secretary General)

constituents⁴. By accepting that test data available for a mixture overrule a classification based on data of its elementary constituents, as proposed by the Organisation for Economic Co-operation and Development OECD³, direct testing appears to get preference over the conventional classification method. Recital 10 of the Preparations Directive 1999/45/EC⁵ reflects this point of view, stating that '...using the conventional methods, it may not be possible to accurately determine the properties of alloys...'. It is further stated hereunder that '...it is therefore necessary to develop a specific method of classification which takes into account their particular chemical properties...'.

In this manuscript, the methodology for aquatic hazard assessment for sparingly soluble metals and metal compounds is taken as a basis to proceed with the hazard assessment for alloys and slags. In doing so, this initially requires so-called dissolution testing, as described in the revised draft OECD guidance document¹. Dissolution testing is defined as 'the determination of the rate and extent to which metals and sparingly soluble metal compounds can produce soluble bio-available ionic and metal-bearing species in aqueous media under a set of standard laboratory conditions representative of those generally occurring in the environment'. This test procedure has found general acceptance for metals and metal compounds as exemplified by studies with Zn powder⁶, CuO powder⁷, CdS, Cd pigment, PbO, Pb₃O₄, CoS massive, CoO powder, Sb₂O₃⁸.

For metals and sparingly soluble metal compounds, the second step is the comparison of the concentration of bioavailable forms being produced during dissolution testing with adequate standard

ecotoxicity data as determined with the soluble metal salt^{1,9}. However, it is well-known that these literature data often show a large variability as physico-chemical test conditions can seriously affect the outcome of ecotoxicity tests^{10,11}. This complicates the comparison between dissolution data with literature data for metals. Copying the second step may find further objection for alloys and slags since, for these materials, dissolution testing may result in simultaneous presence of several soluble metal forms (mixtures!) and the possibility for synergetic and antagonistic ecotoxicological mechanisms.

For reasons stated above, the direct evaluation of the solution (rendered after dissolution testing) should be promoted, by noting effects on organisms added to it.

This study aims at exemplifying the proposed aquatic hazard assessment strategy for alloys and slags, being the result of, and being in line with the considerations given above.

TRANSFORMATION - DISSOLUTION PROTOCOL : ALLOYS PROPOSAL

Dissolution tests are performed in different phases. In a first phase, 24 hour screening tests at a loading of 100 mg/l are applied. Subsequent tests that might need to be performed consist of dissolution testing during a 7-day period at a loading of 100, 10 and 1 mg l⁻¹ respectively. The decision to proceed to the next step depends on whether the resulting dissolved element concentration exceeds a (pre-defined) cut-off value, the latter being based on reported ecotoxicity data of the element of concern, tested as a soluble salt (Fig. 1.). Alternatively, direct ecotoxicological evaluation may be applied for solutions rendered after dissolution testing.

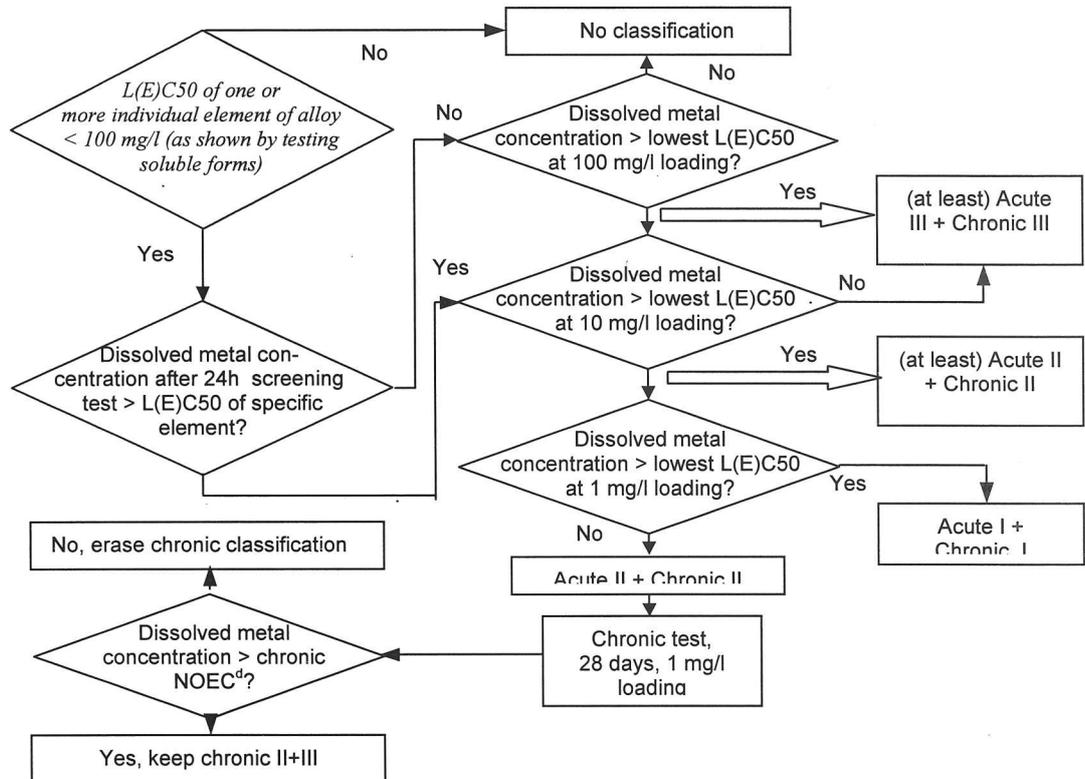


Figure 1 -The tiered approach proposed for the assessment of classification for alloys

TEST MATERIALS

The following test products were applied: 'FeV alloy', 'FeMo alloy', 'HCFeCr alloy' and a 'HCFeCr slag'. Each test material was a mixture blended from samples provided by different manufacturers. All materials were prepared, monitored for certain physical parameters, mixed and supplied by SINTEF

Civil and Environmental Engineering. The mean grain size of the tested materials were: 702 μ m for the FeV alloy, 671 μ m for the FeMo alloy, 556 μ m for the HCFeCr alloy and 705 μ m HCFeCr slag. At least 77 volume percentage of all test materials were between a 100 μ m and 1000 μ m particle diameter¹². Chemical composition is summarised in Table 1.

HCFeCr-slag (composition in %)

Cr ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	MgO	CaO	TiO ₂	Ni	C	S	Co	Mn	Cu	Zn	As,Cd	Pb
7.1	3.3	29.2	24.7	30.2	2.2	0.5	0.05	0.7	0.2	0.005	0.2	0.002	0.1	<0.0002	<0.001

HCFeCr-alloy (composition in %)

Cr	Fe	Si	Al	Mg	Ca	Cu	Ti	Ni	Co	V	S	C	P	Mn	Zn
57.8	28.2	3.7	*	*	*	*	0.14	0.33	0.04	0.14	0.02	7.6	0.02	0.2	*

FeMo-alloy (composition in %)

Mo	Fe	Cu	Al	Ni	Cr	Pb	Si	C	S
69.35	28.7	0.37	<0.01	0.17	0.043	0.004	0.80	0.03	0.07

FeV-alloy (composition in %)

V	Fe	Al	Ni	Cr	Pb	Si	P	Mn	Cu	C	S
80.27	15.79	0.48	0.016	0.084	0.012	0.92	0.018	0.46	0.10	0.2	0.018

Table 1 – Measured chemical composition of the test materials. * = Not Determined

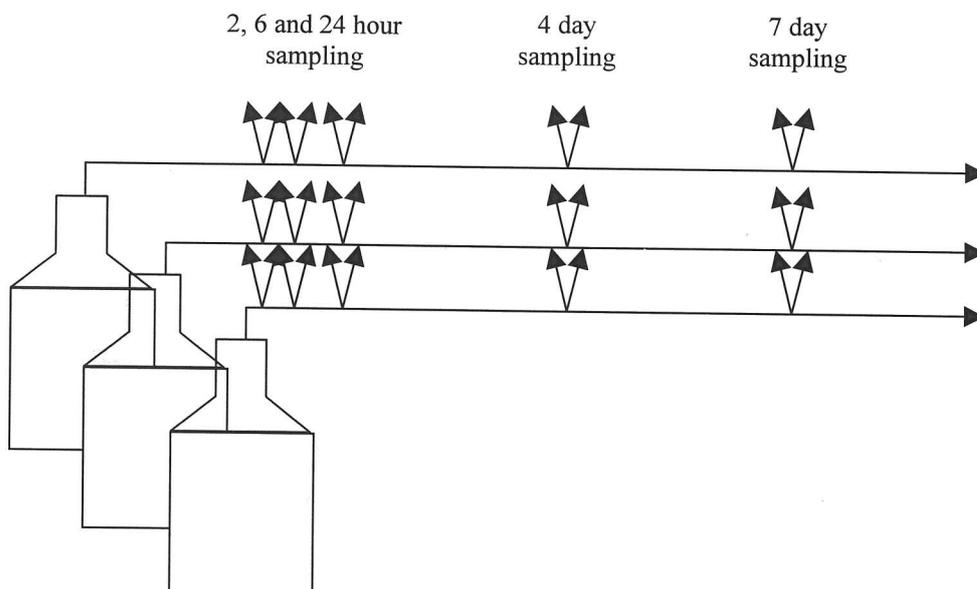


Figure 2 - Acute transformation – dissolution testing. Test set-up.

ALLOY & SLAG TRANSFORMATION DISSOLUTION TESTING

The different test materials were initially tested in 24 hour screening tests at a loading of 100 mg/l. Dissolved concentrations were low from an ecotoxicological perspective and will not further be addressed in this manuscript. Subsequently, 7-day acute tests at a loading of 100 mg/l were performed. The test performance is pictured in Fig. 2. The tests were done in glass bottles cleaned with HCl and subsequently rinsed with demineralised water. Before starting the acute dissolution tests, the products were homogenised by means of a mixing device (turbula T2C). For each test material, 100 mg was added to each of three different test bottles.

1 litre ISO 6341 medium^b was added to each test vessel. All suspensions were continuously mixed on laboratory shakers

^b Chemical composition of ISO 6341 medium is NaHCO₃ : 65.7 mg.l⁻¹; KCl : 5.75 mg.l⁻¹; CaCl₂.2H₂O; 294 mg.l⁻¹; MgSO₄.7H₂O : 123 mg.l⁻¹

(100 ± 20 rpm) at ambient temperature (22 ± 2°C), in the dark. The test vessels were closed, not buffered with CO₂. This application is referred to as “air-buffered”.

At different time intervals (2 and 6 hours, 1, 4 and 7 days), the pH, temperature and dissolved oxygen concentration were measured in each test vessel.

Additionally, samples were taken from each test jar (in duplicate) for element analysis with Inductive Coupled Axial Plasma Emission Spectrometry (ICAP). Prior to this, the samples were filtered (0.2 µm) and acidified (1% HNO₃) and stored in polyethylene (PE) sample cups, at room temperature. Based on the analytical results for the 7-day sample, it was decided whether samples taken on previous time periods (i.e. 2 and 6 hours, 1 and 4 days) had to be analysed.

ECOTOXICITY TESTING : SET-UP

All filtered (0.2 µm) solutions rendered after transformation dissolution testing went through ecotoxicological evaluation. For

each solution, one particular standard ecotoxicity test was applied. When choosing the ecotox test species, two conditions ought to be fulfilled:

- a standard^c species and a standard protocol should be applied and,
- the test species should be relatively sensitive for the element(s) that went into solution after transformation – dissolution testing.

The sensitivity per taxon and per element needs to be deduced from literature data. In this particular case, alga and fish testing had to be performed applying respectively guideline OECD 201¹³ and OECD 203¹⁵. The test design is summarised in Table 2.

LITERATURE SEARCH : STRATEGY

A literature search was performed for the following elements: Mo, V and Co. Data were collected from several sources : databases (Aquire, Cheminfo, Hazardous Substance Database), individual reports¹⁶. LISEC reports, individual scientific manuscripts.

The available test description were summarised noting:

- the product applied in the ecotoxicity test
- the biological species used,
- the bioassay endpoint (e.g. mortality, reproduction, growth, ...)
- water hardness of medium
- pH range of medium during the test
- the measure of effect (e.g. E_bC50,

^c Under “standard” species, we refer to the species recommended by the OECD guidelines, acute tests (e.g. OECD 201¹³, OECD 202¹⁴ and OECD 203¹⁵)

E_rC50, LC50, NOEC, LOEC^d)

- effect concentration reported with confidence interval whenever possible, ...

The adequacy of data was evaluated against well-described “quality and applicability” criteria. These criteria are comparable with the “reliability and relevance” criteria as defined by the Environmental Protection Agency (EPA)¹⁷ and RIVM¹⁸. Hence, in order to select literature data especially useful for comparison with the rendered element concentrations after dissolution testing, the “quality and applicability” criteria gave more weight to:

- data applicable to standard species
- tests performed in a medium with water hardness similar to the ISO 6341 medium
- LC50 and EC50 data instead of NOEC and LOEC data
- effect concentrations expressed as actual instead of nominal values.

A more detailed discussion on the criteria to be applied and the categorising of data can be found elsewhere¹⁹. For “quality and applicability” categories, well-described criteria, were defined for the taxa Pisces, Alga and Crustacea. This allowed the allocation of individual data into four categories as shown below in Table 3.

Quality / applicability code
I (high quality / applicability)
II (moderate quality / applicability)
III (low quality / applicability)
IV (not useful)

Table 3 - Quality / applicability criteria

^d E_bC50 / E_rC50 = concentration resulting in a 50% biomass /growth rate inhibition in comparison with the control, LC50 = concentration resulting in a 50% mortality, NOEC = No Observed Effect Concentration, LOEC = Lowest Observed Effect Concentration

Solution after dissolution test with	Test species	Test concentrations % (as a % of the solution rendered after dissolution testing)	Medium	Exp. period (hrs)	Replica's
HCFeCr – alloy	<i>Raphidocelis subcapitata</i>	90, 50, 25, 12.5, 6.25	As recommended in OECD 201, with EDTA	72	3
FeMo – alloy	<i>Raphidocelis subcapitata</i>	90, 50, 25, 12.5, 6.25	As recommended in OECD 201, with EDTA	72	3
FeV- alloy	<i>Danio rerio</i>	100, 50, 25, 12.5, 6.25	ISO 6341	96	1 (7 fish)
HCFeCr – slag	<i>Danio rerio</i>	100, 50, 25, 12.5, 6.25	ISO 6341	96	1 (7 fish)

Table 2 - Summary of test design ecotoxicity testing

RESULTS TRANSFORMATION – DISSOLUTION TESTING

Dissolution testing with the 'HCFeCr-slag' did not result in any dissolved^e element in the resultant solution. Testing with the 'HCFeCr-alloy' revealed traces of cobalt and vanadium (1 µg/l). For the 'FeV-alloy', the dissolution is almost entirely restricted to vanadium (831 µg/l) with some traces of aluminium (22.3 µg/l). For the 'FeMo-alloy', the dissolution is almost entirely restricted to molybdenum (8.25 mg/l) with some traces of nickel (18.2 µg/l). See Table 4 for detailed results. The dissolution pattern for vanadium appeared to obey different kinetics for the test vessels applied (N=3). For one test vessel,

an apparent linear increase of dissolved vanadium was demonstrated. The dissolution kinetic can be written as: $\text{mg V.l}^{-1} = 0.127t - 0.0072$ ($R^2 = 0.999$). For the two other test vessels, a first order kinetic appeared to be more appropriate and could be averaged as: $\text{mg V.l}^{-1} = 1.306 (1 - e^{-0.141t})$. Given the relatively small number of data points used this apparent anomaly cannot be said to be significant at this stage. A linear increase of dissolved molybdenum was demonstrated over the test period of 7 days. The dissolution kinetic can be described by the following equation: $\text{mg Mo.l}^{-1} = 1.185t - 0.0295$ ($R^2 = 0.999$).

	FeV alloy	FeMo alloy	HCFeCr alloy	HCFeCr slag
V (mg/l)	0.831	ND	0.001	ND
Ni (mg/l)	<0.005	0.0182	<0.005	<0.005
Al (mg/l)	0.0223	<0.015	ND	<0.015
Mo (mg/l)	ND	8.25	ND	ND
Co (mg/l)	ND	ND	0.0007	<0.001
Cr (mg/l)	<0.006	<0.006	<0.006	<0.006
Cr ⁶⁺ (mg/l)	ND	ND	ND	<0.035
Cu (mg/l)	ND	<0.0025	ND	<0.0025
Mn (mg/l)	ND	ND	ND	<0.001
SiO ₂ (mg/l)	ND	ND	ND	<0.1
As (mg/l)	ND	ND	ND	<0.005
Zn (mg/l)	ND	ND	ND	<0.006
Pb (mg/l)	<0.006	<0.006	ND	<0.006
Fe (mg/l)	<0.050	<0.050	<0.050	<0.050
Cd (mg/l)	ND	ND	ND	<0.0012

Table 4 - Average concentrations samples taken at the end of the 7-day tests. (ND = Not Determined)

^e Dissolved defined as not withdrawn by a 0.2 µm cellulose filter

RESULTS ECOTOXICITY TESTING

Data resulting from ecotoxicological evaluations of media accomplished after 7-day dissolution testing are summarised in Table 5. For all performed short-term tests, it can be concluded that no ecotoxicological effects were demonstrated. For alga tests, some minor stimulation effects occur (t-test, $p < 0.05$) when comparing control test solutions and highest test concentration.

RESULTS LITERATURE STUDY

The discussion given below is based on a more extensive report¹⁹.

Molybdenum. Data were found for three species of freshwater alga : *Scenedesmus subcapitata*, *Chlorella vulgaris* and *R. subcapitata*. Specific analyses were only reported in tests performed with *R. subcapitata*²⁰ resulting in a high quality/applicability (code I). No important toxicity was reported here ($>36.1 \text{ mg Mo l}^{-1}$).

Eight data were found for the crustacean *Daphnia magna* (code I – IV). Test condition data (water hardness and pH) were

not always available and specific analyses were either not performed or it is unsure whether Mo analyses were performed. This may explain the variability in reported effect concentrations for *D. magna*. Overall, the toxicity to *D. magna* appears to be low, at least above $36.36 \text{ mg Mo per l}^{21}$.

Oncorhynchus mykiss and *Pimephalus promelas* appear to be the most intensively investigated fish species. Data for *Danio rerio* were not found. Overall, ecotoxicity to fish appears to be low (at least $>36.9 \text{ mg Mo l}^{-1}$).

Vanadium. Data were found for at least one freshwater alga species : *Chlorella vulgaris*. The alga test species used according to the OECD 201 guideline, with four different vanadium containing materials, is not known²². Data in this study are probably expressed as actual concentrations. The lowest EbC50 reported for the short-term tests was 1.77 mg V per l (probably code I).

Several data were found for the crustacean *D. magna*. 7 Values exist mentioning E(L)C50 data for *D. magna*, exposure period 48 hours (code I - III). The range of effect

Solution resulting after dissolution test with :	Test species	pH range during test	Highest metallic element concentrations found in the strongest test solution	Test result
FeMo - alloy	<i>Raphidocelis subcapitata</i>	8.00 - 9.23	Mo : 7.77 mg/l; Al : 0.063 mg/l; Ni : 0.022 mg/l	8.4% growth stimulation in 90% test concentration in comparison with control
HCFeCr - alloy	<i>Raphidocelis subcapitata</i>	8.00 - 9.30	All below detection limit	13.2% growth stimulation in 90% test concentration in comparison with control
FeV - alloy	<i>Danio rerio</i>	7.95 - 8.30	V : 0.652 mg/l; Fe: 0.157 mg/l; Al : 0.028	No mortality in either test solution
HCFeCr - slag	<i>Danio rerio</i>	7.90 - 8.27	All below detection limit	No mortality in either test solution

Table 5 - Summary of results for ecotoxicological evaluations of media rendered after transformation dissolution testing

concentrations is 1.52 – 17.21 mg l⁻¹.

Literature reports ecotoxicity testing with six fish species: *Salmo gairdneri*, *Poecilia reticulata*, *O. mykiss*, *P. promelas*, *D. rerio* and *Cyprinus carpio*. LC50_{96h} values show variation. For example for *S. gairdneri*, LC50_{96h} values range from 5.2 to 118 mg V l⁻¹ (N=10, code III data). Interspecies difference in sensitivity is most clearly demonstrated by Beusen & Neven (1987)²³. The range of reported LC50 96 hours data found for *P. promelas* and *C. carpio* are respectively 1.85 – 55 mg V l⁻¹ and 1.24 – >16.78 mg V l⁻¹.

Cobalt. Data were found for two freshwater alga species: *C. vulgaris* and *R. subcapitata*. Three high quality/applicability data (code I) values exist for *R. subcapitata*: E_bC50 72-hours 0.043, 0.09 and 0.07 mg Co l⁻¹. The third result was generated from a toxicity test with the sparingly soluble Co₃O₄ compound and was expressed as a nominal Co concentration. However, the test solutions were prepared based on a saturated Co₃O₄ solution from which the final estimated Co concentration was derived.

Data referring to crustaceans were reported by Indeherberg & Brouwers (2000)¹⁹. However, only 8 *D. magna* EC50_{48h} data carry code I - III. For these, toxicity endpoints range from 1.11 – 3.2 mg Co l⁻¹. One value entirely falls outside this range (>100 mg Co l⁻¹) which is most likely the result of applying the sparingly soluble Co powder in combination with the lack of specific analyses.

The following fish species have been investigated: *O. mykiss*, *P. promelas*, *D. rerio* and *C. carpio*. No information on concentrations and water hardness measurements were available. The variation of the reported toxic concentration is quite

large (> a factor 200). Even for the only two code III studies reporting LC50_{96h} effect concentrations, a huge difference in effect concentrations existed (1.41 versus >100mg l⁻¹), which is probably due to the different application form of Co (Co powder versus CoCl₂·2H₂O). In terms of dissolved Co, the toxicity of Co to fish is probably situated in the lower mg l⁻¹ range.

DISCUSSION AND CONCLUSIONS

The results have shown that traces of elements other than the bulk elements may go into solution, indicating that, also for other alloys, practical testing according to the dissolution protocol should be considered. Skaeff and King (1999)²⁴ also stressed the need for actual testing of alloys. They demonstrated that the results of alloy dissolution testing cannot be predicted by dissolution testing of a metal powder mixture with a composition similar to the alloy of concern.

The dissolution kinetic for molybdenum, as for the FeMo-alloy, and vanadium, as for the FeV-alloy, appeared to follow a linear pattern. First order kinetic dissolution patterns are the general rule and a linear increase is observed occasionally²⁵. The OECD draft protocol for dissolution testing of metals and metal compounds¹ requires curve fitting for accomplished data in order to determine the applicability of e.g. a linear, first order or second order kinetic. This may point out that interest exists in the extrapolation of data towards longer dissolution periods (> 7 days). Special attention might indeed be required for test materials showing a steady increase of elements as a result of dissolution testing. However, the same protocol¹ specifies that the highest observed concentrations should be compared with ecotoxicity cut-off values. The latter appears to ignore whatever the result of curve fitting revealed.

thermal shock parameter $R'st$ is calculated by the equation:

$$R'st = \sqrt{\frac{\lambda^2 G_F}{E\alpha^2}}$$

where

- λ = Thermal conductivity
- G_F = Fracture energy measured under controlled crack propagation
- E = Young's modulus of elasticity
- α = Coefficient of thermal expansion

The improvement of the electrode material can be demonstrated by use of the electrode simulation models, with the new material properties.

The case with thermal stresses following a shut down, as shown in Figure 4, has been used again, but now we have compared the stresses in the two cases: regular and improved electrode material, Figure 10.

Reduced stresses mean that the risk of having a breakage in the baked part is considerably reduced. This will shorten the recovery time and improve furnace throughput.

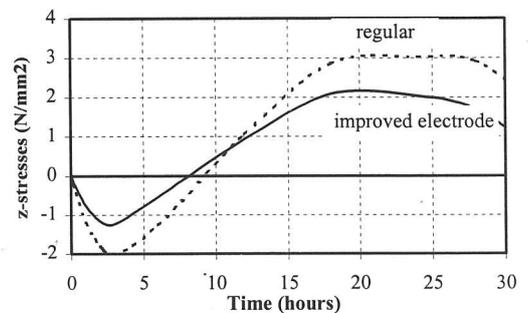


Figure 10 - Effect of an improved electrode and thermal stresses during 12 hours current recovery. See also Figure 4.

7 CONCLUSIONS

A safe and reliable electrode operation does include consistent electrode products, good electrode casing design and control, proper electrode equipment and operating procedures.

To maintain current knowledge about the Søderberg electrode operation and to maintain good operating routines and procedures, it is necessary to have regular staff training sessions.

Electrode simulations, various electrode measurements, and electrode surveys are all helpful tools in the work for improved electrode performance and the analyses for the reasons behind any specific problem.

References

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