IRON(II)-SULFATE AS CONCRETE ADMIXTURE FOR CHROMIUM(VI) REDUCTION

EISEN(II)-SULFAT ALS BETONZUSATZMITTEL ZUR CHROM(VI) - REDUZIERUNG

SULFATE DE FER(II) EN TANT Q'ADJUVANT POUR BETON POUR LA REDUCTION DU CHROME(VI)

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SUMMARY

Studies for an approval have been carried out using iron (II)-sulfate in order to introduce a new type of concrete admixture. Iron(II)-sulfate is supposed to reduce soluble chromium(VI) in cement. The behaviour of two modifications was tested in grout and mortar regarding compatibility, harmlessness and efficiency. It is shown that there is a certain influence on the properties of cement but the requirements are fulfilled. The efficiency could be proved but depends on the storage period for one of the modifications.

ZUSAMMENFASSUNG

Im Rahmen der Zulassung einer neuen Betonzusatzmittelgruppe wurden Versuche mit Eisen(II)-Sulfat durchgeführt. Eisen(II)-Sulfat soll das lösliche Chrom(VI) im Zement reduzieren. Untersucht wurde das Verhalten im Zementleim und Mörtel an zwei Modifikationen im Hinblick auf Verträglichkeit, Unschädlichkeit und Wirksamkeit. Es wird gezeigt, daß zwar ein merkbarer Einfluß auf die Zementeigenschaften vorhanden ist, die Anforderungen aber erfüllt werden und daß die Wirksamkeit gegeben, bei einer Modifikation aber von der Lagerung abhängig ist.

RESUME

Dans le cadre de l'approbation d'un nouveau groupe d'adjuvants pour béton, des études ont été réalisées sur le sulfate de fer(II). Le sulfate de fer(II) réduit le chrome(VI) soluble contenu dans le ciment. L'effet de deux modifications sur le coulis et le mortier est analysé quant à la compatibilité, le caractère inoffensif et l’efficacité. Il est démontré que cet adjuvant a une influence sur les propriétés du ciment, mais que les exigences sont respectées. L’efficacité est prouvée, mais elle dépend de la période d’emmagasinage.

Keywords: concrete admixture, chromium, skin allergies, reducing agents, iron(II)-sulfate, corrosion, cement properties

1 INTRODUCTION

According to extensive Danish investigations, the content of soluble chromium(VI) in cement has a non-neglectable influence on the formation of skin allergies (bricklayer or cement eczema). After a contact with skin for many years, a sensitization of skin may appear so that even low quantities of chromium(VI)-ions may produce allergies (Avnstorp, C. (1992) and Jaeger, H.; Pelloni, E. (1950)). For this reason the Senate Committee for testing health-harming working products has included chromium(VI) into the list of contact allergens. In Germany, chromium(VI)-allergy is recognized in the Berufskrankheiten-Verordnung as a occupational disease caused mainly by cement.

According to investigations of Pisters (1966) the content of soluble chromium(VI) of German cements lies between 0 and about 30 ppm. The German Technische Regeln für Gefahrstoffe (1993) as well as the relevant Danish regulations regard a content of soluble chromium(VI) of up to 2 ppm as harmless.

As chromium-compounds mainly result from raw materials which were used for the production of cement, no direct influence may be taken during production upon the content of chromium(VI) in cement.

Therefore the use of reducing agents was discussed. When using these agents in concrete technology some questions result, above all the influence on cement properties and the influence of the storage period on efficiency.

Especially for the use in a construction material such as cement a certain storability is the condition for an problem-free application. According to the indications of the Bau-Berufsgenossenschaften, approximately 86% of the cement is used within a few weeks. The remaining 14% were stored in bags for a longer time. Only this part of the cement production is used on small building sites. In this case, the contact with fresh concrete containing chromium(VI) is more probable than on big building sites, where the transport and application of concrete is hardly done by hand.

Another point which has to be taken into account for the use of iron(II)-sulfate is the question of a possible influence on the technical properties of cement, mortar and concrete. The influence on the properties of cement, mortar and concrete was hardly investigated till now in comparison to the reducing effects.

2 REDUCTION OF CHROMIUM(VI)

2.1 Survey

The elimination of chromium(VI) by technical means, such as exposure to a temperature of 1400°C for 3 hours or the abstraction of oxygen during the production of clinker, is not possible without influencing essential properties of cement.

As an elimination by technical means may not be exploited only the chemical reduction of chromium(VI) remains.

In a suspension of cement, iron(II)-sulfate and water, the main chemical reaction takes place according the following equation

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+}$$
$$Cr^{VI} \rightarrow Cr^{III}$$

Table 1 gives a survey of possible reducing agents together with their dosage and the remaining content of chromium(VI) introduced by S. Fregert and B. Gruvberger (1973). The cement used had a content of soluble chromium(VI) of approximately 15 ppm.

Table 1: Chemical agents for the reduction of chromium(VI)

Name	Chemical Formula	Dosage Percentage by mass of cement	Cr(VI)-content after reduction[1)] [ppm]
Ascorbic acid	$C_6 H_8 O_6$	5	6
Sodium thiosulfate	$Na_2 S_2 O_3$	5	9
Sodium dithionite	$Na_2 S_2 O_4$	0,2	0
Sodium metabisulfit	$Na_2 S_2 O_5$	5	9
Iron(II)-sulfate	$FeSO_4 \cdot 7H_2O$	0,10 to 0,25	0
Iron(II)-ammonium sulfate	$(Fe(NH_4)_2(SO_4)_2 \cdot 6H_20$	0,25 to 0,50	0

[1)] soluble chromium (VI) in the cement was about 15 ppm

It becomes evident that most of the indicated reducing agents need a far too high dosage and yield very poor results. Sodium dithionite, which achieves a complete reduction by adding 0,2 % by mass, is not storable in humid surroundings.

Only iron(II)-sulfates achieve, even at low dosage, a complete reduction of chromium(VI).

2.2 Iron(II)-sulfate

Especially in Scandinavia and the former GDR, as well as in the FRG, iron(II)-sulfate has succeeded as reducing agent. In this field most dermatological and technical investigations have been carried out.

Iron(II)-sulfate is obtained from the production of titanium dioxide. Milled iron titanium ore (for instance ilmenite $FeTiO_3$) is broken down with sulfuric acid. During the process iron(II)-sulfate cristallizes and is drawn off as so-called green salt. It is dried down to a residual humidity content of about 4 % by mass. The granulated salt with a content of iron(II)-sulfate of approximately 50 % by mass contains 6 to 7 moles of cristallization water (hexa-heptahydrate). In a further modification hexa-heptahydrate is transformed in a second drying process under the influence of heat and vapour, into a powdery iron(II)-sulfate (about 80 % by mass) with 1 mole of cristallization water (monohydrate).

This second modification, the monohydrate, has been developed in order to extend the storing time. As iron(II)-sulfate is a strong reducing agent, the presence of water and air always involves the risk of oxydation. This shall be avoided by the reduction of the cristallization water content.

3 TESTS ABOUT USABILITY IN CONCRETE TECHNOLOGY

3.1 General

In Germany the use of concrete admixtures is still regarded critically. Problems were seen in the estimation of compatibility, harmlessness and efficiency. That’s why, in the relevant regulations and approval guidelines for concrete admixtures Richtlinien für Betonzusatzmittel (1993), tests for every kind of admixture are laid down.

The compatibility and harmlessness of concrete admixtures have to be estimated in view of the modification of technical properties (setting time and soundness) of cement and a possible influencing of the protection against corrosion (chloride content and electrochemical test). These investigations are uniform for all kind of admixtures with only a few exceptions.

The efficiency of concrete admixtures is determined according to the different functions. The purpose of this test is not a qualification test - this test is anyway required for all approved concrete admixtures when used. It is a general control of defined properties attributed to an admixture, as for instance, for plasticizers and superplasticizers, the reduction of water required for a certain workability or the improvement of the workability itself.

A further aspect for the use of admixtures is the dosage. A minimum dosage should guarantee that the admixture is available in sufficient quantity for being distributed equally in concrete. For the maximum dosage the approval regulations use the term “maximum recommended dosage”. While applying, this dosage may not be exceeded without a special permission. The harmlessness of the admixture is controlled with twice the maximum recommended dosage; the requirements to efficiency must be fulfilled by a dosage between the maximum and minimum dosage.

For the hexa-heptahydrate a maximum recommended dosage of 5 g/kg cement (0,5 % by mass) is scheduled. On behalf of the higher effectiveness to be expected for the monohydrate this quantity has been reduced to 3 g/kg (0,3 % by mass).

In the Otto-Graf-Institute, investigations about the compatibility, corrosion problems and the applicability of iron(II)-sulfate were carried out with both modifications (hexa-heptahydrate and monohydrate).

3.2 Compatibility with cement

On behalf of the variety of cement types in Germany it is not sufficient to determine the compatibility only upon a single cement. Already in the earlier editions of DIN 1164 (1958), even cements with slag or trass, except portland cement, are indicated. Owing to official approvals during the last years cements were admitted which contained fly ash, limestone or puzzolanes in different compositions. Today most of them are integrated into the new edition of DIN 1164 (1994). Even the different raw material deposits have an influence upon the properties of concrete. Therefore, for an estimation of the compatiblity, an average of 16 cements has been compiled. Upon these 16 cements the influence of an admixture is determined regarding the water required for normal consistency, the influence on initial and final setting by the Vicat-apparatus as well as the influence on the soundness.

The tests were carried out using cement grouts with and without iron(II)-sulfate.

In general, the increase of water required by a concrete additive is not regarded as positive if other properties don’t ameliorate essentially. A need of more water may be compensated by an increased addition of water and, thus, a non-desired increase of the w/c-ratio or by additon of a superplasticizer or plasticizer which increase the costs of concrete.

Fig. 1 shows the influence of iron(II)-sulfate upon the water required by cement. It may be seen that generally the water required for all types of cement is slightly increased. For portland cements of the strength class 32,5 R, the addition of monohydrate seems to require more water than hexa-heptahydrate. The cements with slag-, limestone- or fly ash-addition behave the opposite way. For the two modifications, the need of water may only be reduced for portland-oil-shale-cement and ordinary portland cement of the strength class 42,5 and with regard to the monohydrate even for an ordinary portland cement (32,5).

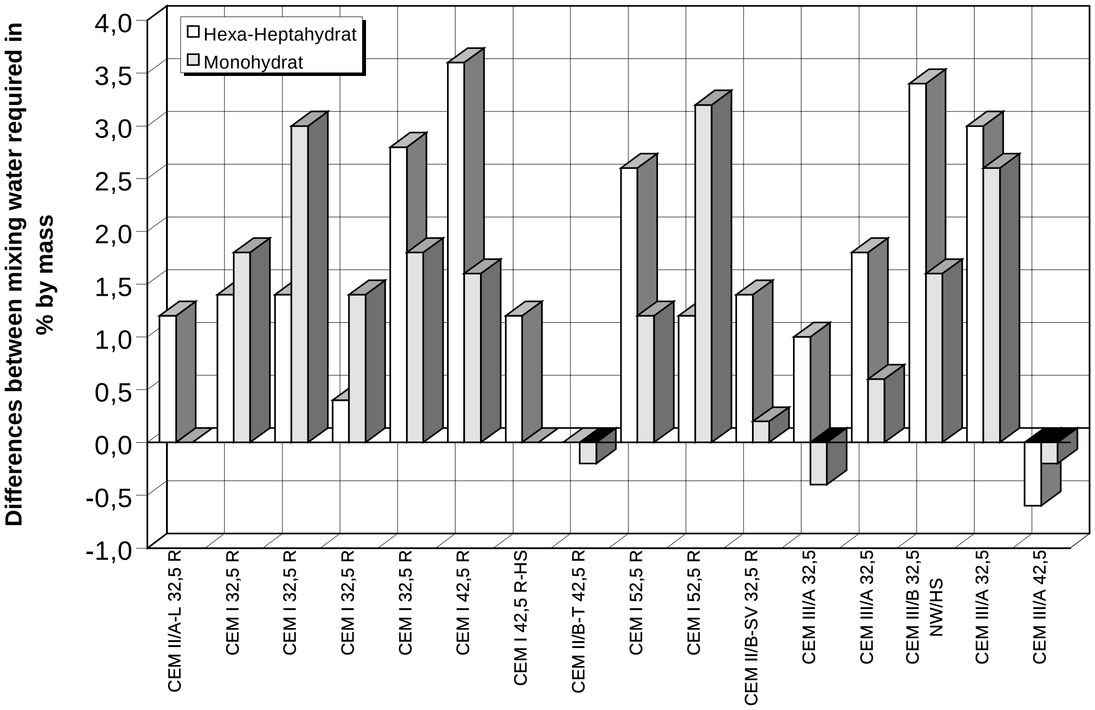

Fig. 1: Influence of iron (II)-sulfate on mixing water required

The setting behaviour is an essential property for estimating the good-naturedness of a matrix. The setting shouldn't start before 60 minutes because, on behalf of the short working time, concrete may be compacted after the beginning of setting, which may later cause structural inhomogeneities of the compacted and hardened concrete. Just as a late setting end normally causes problems, a prolonged storage time increases the susceptibility of concrete to shrinkage cracks (early shrinkage). Therefore the final setting shall not exceed 12 hours.

As Fig. 2 shows, hexa-heptahydrate has retarded the initial setting time of slag cement and portland cement and, in general, accelerated it for higher strength classes. This phenomenon even causes a reverse action (initial setting time after 10 min.) for one cement.

Monohydrate, too, retards the initial setting time in general, but for cements of the upper strength classes it doesn't show the aforementioned problematic behaviour.

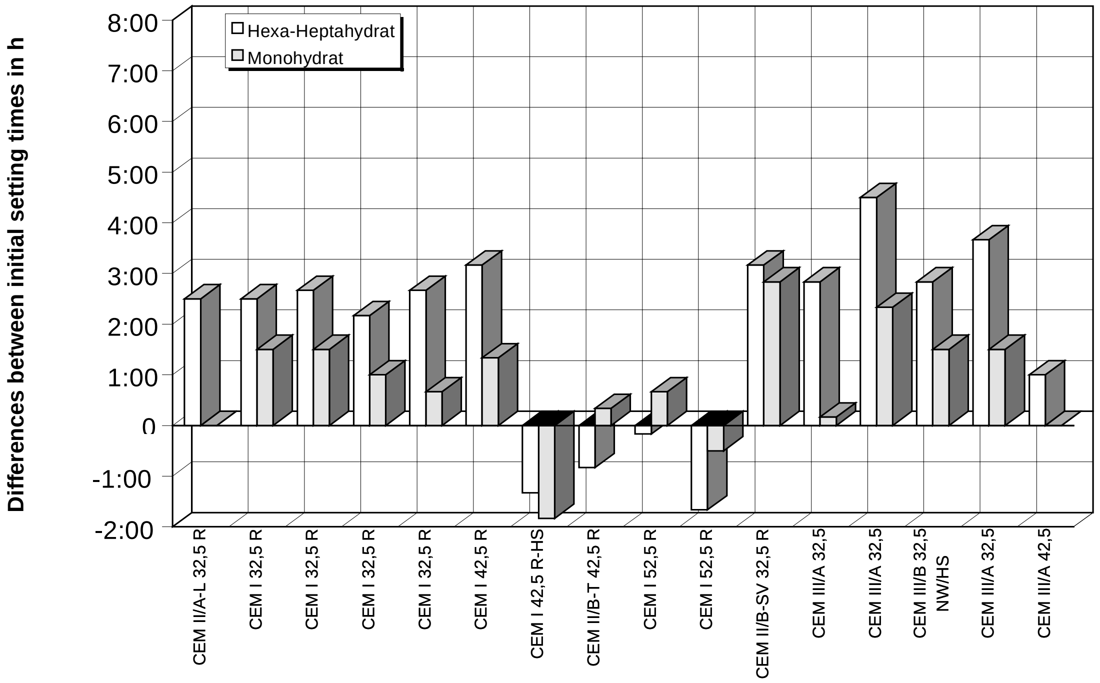

Fig 2: Influence of iron (II)-sulfate on initial setting time

With the exception of portland cement (CEM I 52,5 R) the final setting is retarded for all tests. In this case the retarding influence of hexa-heptahydrate upon the ordinary portland cement becomes most evident (see Fig. 3).

The addition of concrete admixtures shall not cause expansion phenomena of the hardened cement matrix. The volume stability is one of the essential properties of concrete in view of durability and applicability. In contrary to today’s cement standards the influence of admixtures upon the soundness of cement is still determined according to DIN 1164 (1958). The specimens were made of grout, stored during 28 days in water of 20°C and, during this time, controlled in view of cracks indicating expansion phenomena. In the following cement standards, this very extensive test has been replaced by a short term test by boiling the grout specimens at the age of one day. Nevertheless the test according to DIN 1164 (1958) has to be considered as the more rigorous test.

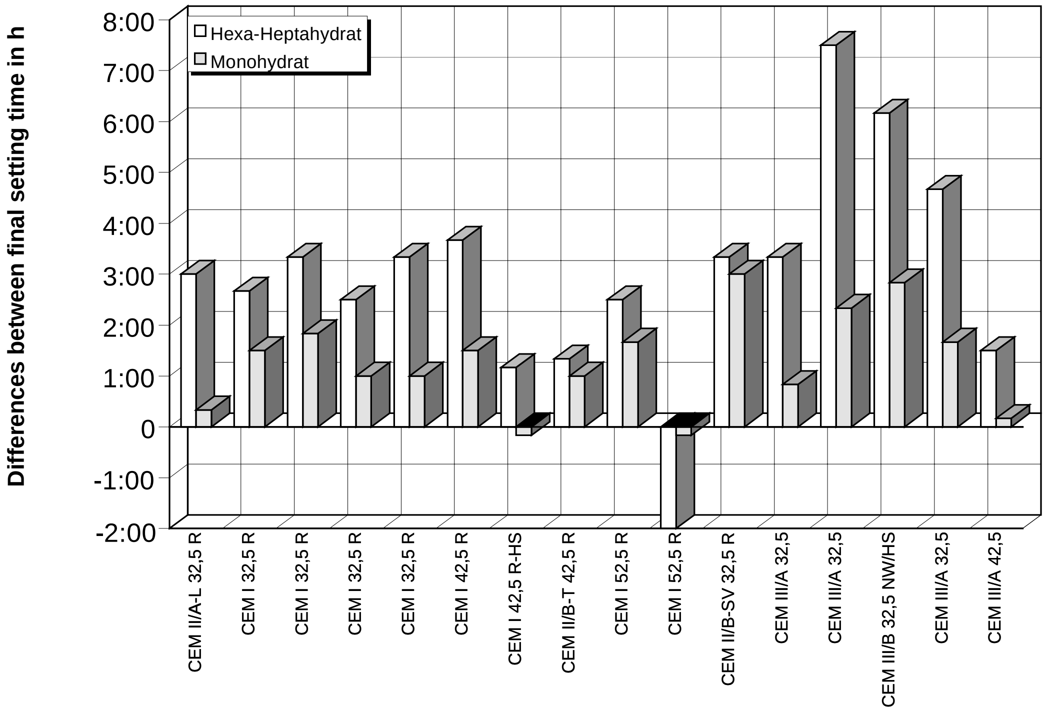

Fig. 3: Influence of iron (II)-sulfate on final setting time

Using the two chromium reducing agents, all specimens were sharp-edged without cracks. Probably owing to early setting (10 min.) CEM I 52,5 R, with hexa-heptahydrate showed shrinkage cracks. Thus, no negative influence could be recognized.

3.3 Corrosion promoting effect

Normally, owing to the high alcalinity of cement matrix, the reinforcing steel in concrete is protected against corrosion. Owing to certain ions reinforcing steel may be polarized to such an extent that local elements appear which may deteriorate the steel. Therefore concrete admixtures shall not contain chlorides, thiocyanates and nitrates as active substances. Concrete admixtures which are used in reinforced concrete shall not contain formiate either.

As the admixtures contain traces of chlorides, or chlorides may enter dissolved in water, the chloride content, in general, is limited to a maximum value of 0,2 % by mass. This requirement is very severe because, under normal conditions, a chloride content up to 0,4 % by mass in concrete is accepted and the admixtures contribute at most 5 % by mass of the cement to the composition of concrete.

With a chloride content of 0,01 % by mass, both modifications were by far underneath the limit value.

In order to exclude other corrosion-promoting agents, unknown until today, in the concrete admixtures, an electrochemical test is required. During the test, the mortar electrode is maintained at a potential of +500mV in relation to the standard hydrogen electrode for a period of 24 hours, using a potentiostat suitable for maintaining this potential without any Ohmic drop. The current necessary for maintaining the potential is registered and, taking into account the surface of the reinforcing steel bar embedded in the mortar electrode, converted into a current density. From the diagram of current density-time-curves experts may conclude if there is a risk of corrosion or not.
The two chromate-reducing agents didn’t show a corrosion-promoting effect.

3.4 Efficiency

The initial purpose of concrete admixtures was to influence and ameliorate the concrete properties by chemical and/or physical effect. This purpose is no longer given for the addition of iron(II)-sulfate. Iron(II)-sulfate doesn’t have an influence on the properties of concrete any longer, but is able to reduce the unhealthy chromium(VI) in cement to a certain extent.

The user of this admixture is interested in the reducing properties as well as in the storability of the iron(II)-sulfate itself and the mixes of cement and iron(II)-sulfate. This is interesting for the reason that most of the endangered persons use cement mixes in sacks. It has to be pointed out once more that sensitization only happens by chromium(VI) which is solved in water and that even the reaction between iron(II)-sulfate and chromium(VI) only happens in watery solution.

In order to be able to estimate the effect of the reducing agent, the chromium(VI) content remaining after a certain reaction time in a cement-water-suspension with iron(II)-sulphate has to be determined. The analyses were carried out according to the Technische Regel für Gefahrstoffe TRGS 613 (1993).

It was intended to investigate the storability of the admixture itself and the storability of the mixes of cement and iron(II)-sulfate, too. For this reason iron(II)-sulfate was tested immediately after removal. Furthermore, mixes with cement were produced which were tested after a storage period of 3 and 6 months in a climate 20/65. The mixes were stored in usual padded envelopes which didn't protect completely against humidity. The iron(II)-sulfate was stored for 3 months tightly closed and tested immediately after opening.

Mixes with cement were produced, too, which were stored for further 3 to 6 months.

As listed in Table 2 , hexa-heptahydrate maintains its excellent efficiency for 6 months. The allowed maximum value of 2 ppm chromium(VI) wasn't reached by far. In contrary, the monohydrate was sensitive against a storage in cement mixes. After 3 months the required reduction of chromium(VI) to 2 ppm was no longer reached.

4 CONCLUSIONS

The tests on iron(II)-sulfate showed that soluble chromium(VI) in cement is reduced to a satisfactory extent. This effect lasted for hexa-heptahydrate for a period of six months when stored in powdery consistence by itself and in mixes together with cement. Although the cement properties were influenced, the requirements for admixtures were fulfilled by far.

Table 2: Content of chromium(VI) in cement with hexa-heptahydrate ($Fe_2SO_4 \cdot 7\ H_2O$) and monohydrate ($Fe_2SO_4 \cdot 1\ H_2O$)

Test material	Storage time of iron(II)-sulfate	Storage time of iron(II)-sulfate/ cement mix	Content of chromium (VI)
	month	month	ppm
Cement	–	–	21,8
Iron(II)-sulfate $Fe_2SO_4 \cdot 7\ H_2O$	0	0	<0,1
	0	3	<0,1
	0	6	<0,1
	3	0	<0,1
	3	3	<0,1
	3	6	0,2
Iron(II)-sulfate $Fe_2SO_4 \cdot 1\ H_2O$	0	0	0,4
	0	3	3,8
	0	6	2,0
	3	0	0,1
	3	3	5,3
	3	6	3,8

5 REFERENCES

Avnstorp, C.: Cement Eczema; An Epidemiological Intervention Study. In: Acta Dermato-Venerologica, 1992, Suppl. 179

DIN 1164 Portlandzement, Eisenportlandzement, Hochofenzement Ausgabe Dezember 1958

DIN 1164-1 Zement-Zusammensetzung, Anforderungen, Ausgabe Oktober 1994

Fregert, S.; Gruvberger, B.: Factors Decreasing the Content of Water-Soluble Chromate in Cement. In: Acta Dermato-Venerologica 53 (1973), pp. 267-270

Jaeger, H.; Pelloni, E.: Tests épicutanés aux bichromates, positifs dans l’eczéma au ciment. In: Dermatologica 100 (1950), pp. 207-216

Pisters, E.: Chrom im Zement und Chromatekzem. In: Zement-Kalk-Gips Nr. 10/1966

Richtlinien für die Erteilung von Zulassungen für Betonzusatzmittel, Fassung Juni 1993

Technische Regeln für Gefahrstoffe TRGS 613 - Ersatzstoffe, Ersatzverfahren und Verwendungsbeschränkungen für chromathaltige Zemente und chromathaltige zementhaltige Zubereitungen, April 1993. In: Bundesarbeitsblatt 4/1993