

Concrete Technology Update

Thiocyanates

Introduction

The use of thiocyanates in chemical admixtures was patented by Master Builders Solutions in 1981. It is well known in the concrete industry that thiocyanates are effective in accelerating the setting of portland cement and enhancing early strength development of concrete. The thiocyanate ion is one of many components in MasterSet[®] FP 20 (formerly Pozzutec[®] 20+) low temperature accelerating admixture with year-round versatility.

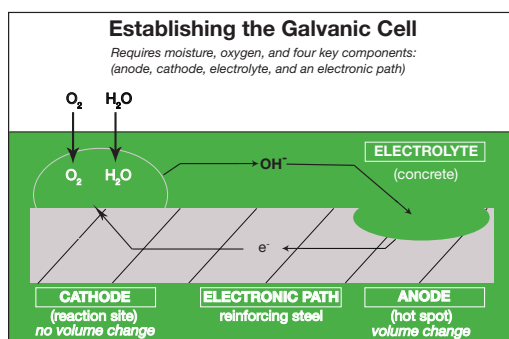
In the late 1980s some concern was expressed over the use of thiocyanates in chemical admixtures. This concern stemmed from a technical report authored by Manns and Eichler¹ that was published in 1982 in an issue of a German concrete journal. In this report, it was stated that the use of thiocyanates in concrete increases the potential for corrosion of reinforcing steel. However, in a paper published in the November 1989 issue of Concrete International² it was shown that thiocyanate-based admixtures are safe for use in reinforced concrete even well beyond their maximum recommended dosages.

The issue of thiocyanates was given a great deal of attention by ACI Committee 212, Chemical Admixtures, and by the American Institute of Architects (AIA). This technology update presents the facts and the position adopted by the technical committees.

Corrosion and Effect of Thiocyanates

Reinforcing steel in concrete is protected from corrosion by a protective or passive film, which is stabilized by the high pH of the concrete environment. This protection exists until a combination of things happen. First, the protective film surrounding the reinforcing steel has to be broken. Second, water and oxygen must both be present around the surface of the reinforcing steel and a galvanic cell has to form. The reinforcing steel then corrodes to form expansive iron oxides. This is the rust that is associated with reinforcing steel corrosion. A schematic diagram that illustrates the corrosion process is shown in Figure 1.

Figure 1.



It is well known that when chloride ions (Cl⁻) are present in sufficient quantities in concrete, they accelerate the corrosion process by destroying the protective film on the surface of the reinforcing steel. The introduction of the first thiocyanate-based admixture to the market in the early 1980s prompted Manns and Eichler to investigate its effect on the corrosion potential of steel in concrete. The thiocyanate ion is believed to behave in a manner similar to the chloride ion. Thiocyanate ion concentrations as high as 2.0 percent by mass of cement were used. It should be noted that **no thiocyanate-based admixtures were used in this study.**

In their report, Manns and Eichler presented data showing that at high concentrations, thiocyanate ions have the potential to initiate the corrosion of reinforcing steel in concrete. Test series utilizing a galvanostatic electrochemical procedure and non-electrochemical aging specimens indicated that the critical concentration for the thiocyanate ion, above which corrosion was likely to occur, was approximately 1.0 percent by mass of cement.

Below the critical concentration, the data indicated that thiocyanates are safe. The authors advocated that care should be taken when thiocyanates are used in chemical admixtures.

Since 1982, many other independent laboratories, as well as Master Builders Solutions, have evaluated thiocyanate-based admixtures in corrosion studies. Table 1 (extracted from Reference 2) presents a summary on the data from these studies on thiocyanates. These data indicate that the threshold level for thiocyanate ions lies between 0.50 and 0.70 percent by mass of cement. For comparison, a 90 fl oz/cwt (5,870 mL/100 kg) dosage of MasterSet FP 20 admixture contains less than 0.165 percent thiocyanate ion concentration by mass of cement (See Table 2). As indicated in Table 1, there was no evidence of accelerated corrosion activity in any of the evaluations that used thiocyanate at a conventional admixture dosage.

An important aspect to remember is that long-term exposure of test specimens at Master Builders Solutions laboratories has consistently shown no difference in corrosion activity between untreated and admixture-treated concretes. This again indicates that thiocyanate-based admixtures are safe for use at recommended dosages.

Current Activities in ACI 212 and the AIA

When the AIA wrote their 1987 edition of Masterspec® Section 03300, "Cast-in-Place Concrete," thiocyanate-based admixtures were not allowed. However, after a review of data obtained from the large number of evaluations initiated after publication of the German paper, the AIA has since updated this specification. There is no mention of thiocyanate-based admixtures in this specification section.

In ACI PRC-212.3³ the following wording appears:

"The fact that an accelerating admixture does not contain significant amounts of chloride, however, does not necessarily render it noncorrosive; for example,

Mann and Eichler (1982) report that thiocyanates may promote corrosion. Nmai and Corbo (1989), however, found that the threshold level for initiation of corrosion by sodium thiocyanate lies between 0.75 and 1.0% by mass of cement, and concluded that the use of sodium thiocyanate-based accelerating admixtures is safe for reinforced concrete applications up to these concentrations. Typical dosages of accelerating admixtures containing sodium thiocyanate contribute between 0.05 and 0.1% sodium thiocyanate by mass of cement, and extremely high dosages may contribute as much as 0.2% sodium thiocyanate. Users may request that suppliers of admixtures containing sodium thiocyanates provide test data regarding the corrosion of steel in concrete. The information should include corrosion results within the intended dosage range."

Table I. Summary of sodium thiocyanate (NaSCN) corrosion studies (Table from Reference 2)

Test Lab	Type of Test Conducted	NaSCN Concentration* % by mass of cement	Results of Study
Manns and Eichler	Electrochemical (galvanostatic)	0 – 2.8	Threshold lies between 1.1 and 1.4% by mass of cement from current density vs. potential data.
	Electrochemical (potentiostatic)	0 – 2.8	No indication of corrosion below 2.8% by mass of cement.
	Aging	0 – 2.8	No rust spot observed below 1.4% by mass of cement.
CTL (PCA)	Stratfull	0, 0.067, 0.135, 0.270	No difference in average time-to-corrosion
Wiss, Janney, Elstner Associates, Inc.	Southern Climate	0, 0.055	Admixture decreased rate of corrosion of reinforcing bars compared to plain control
Webster Engineering	Southern Climate (de-ionized water)	0, 0.055, 0.090	No corrosion activity.
Solar Testing, Inc.	Modified Southern (same slump)	0, 0.045, 0.135 0.203, 0.271	Admixture-treated specimens exhibiting less corrosion activity compared to plain control
Master Builders Solutions	Modified Southern Climate (same w/c) (de-ionized water)	0, 0.203	No corrosion activity.
	Electrochemical (galvanostatic) (screened mortar)	0 – 1.0	Threshold lies between 0.75 and 1.0% by mass of cement.
	Stress-Corrosion Cracking	0.203	No stress-corrosion cracking of low-relaxation and stress-relieved prestressing wires.
activity.	Long-term outdoor	0, 0.045, 0.067, 0.203	No difference in corrosion

* Thiocyanate ion (SCN-) is 71.6 percent of NaSCN to mass. Therefore, a concentration for NaSCN of 2.8% by mass of cement would indicate a concentration for thiocyanate ion of 2.0% by mass of cement.

Table 2. Sample Calculations of Thiocyanate Ion Contribution of MasterSet FP 20 Admixture

Thiocyanate Ion Content:	Less than 2%	
Maximum Dosage:	90 fl oz/cwt	(5,870 mL/100 kg)
Weight:	11.74 lb/gal	(1.41 kg/L)
Maximum Thiocyanate Ion Content of Concrete:	< 0.165 lb/cwt < 0.165% by mass of cement	

$\left[\frac{90 \text{ fl oz}}{\text{cwt}} \right]$	$\left[\frac{11.74 \text{ lb}}{\text{gal}} \right]$	$\left[\frac{1 \text{ gal}}{128 \text{ fl oz}} \right]$	$\left[0.02 \right]$	< 0.165 kg/100 kg < 0.165% by mass of cement
$\left[\frac{5.87 \text{ L}}{100 \text{ kg}} \right]$	$\left[\frac{1.41 \text{ kg}}{\text{L}} \right]$	$\left[0.02 \right]$		

Conclusions

1. The thiocyanate ion is non-corrosive at the concentrations found within current recommended dosage ranges of Master Builders Solutions' thiocyanate-based admixtures.
2. Should an architect or engineer desire to include a limitation on the amount of thiocyanates in concrete, the wording shown in the suggested specification below is recommended.

Suggested Specification Language for Thiocyanate-Based Admixtures

Thiocyanate-based chemical admixtures meeting the requirements of ASTM C494/C494M shall further comply with the following:

When used at the manufacturer's maximum recommended dosage, thiocyanate ions contributed from the admixture shall not exceed 0.30 percent by mass of cement.

The manufacturer shall certify that thiocyanate-based chemical admixtures proposed for use on this project meet this requirement.

References

1. Manns, W., and Eichler, W.R., "The Corrosion-Promoting Action of Concrete Admixtures Containing Thiocyanates," *Betonwerk + Fertigteile-Technik* (Wiesbaden), V.48, No. 3, 1982, pp.154 - 162.
2. Nmai, C.K. and Corbo, J.M., "Sodium Thiocyanate and the Corrosion Potential of Steel in Concrete and Mortar," *Concrete International: Design & Construction*, V. 11, No. 11, Nov. 1989, pp. 59 - 67.
3. ACI PRC-212.3 Report on Chemical Admixtures for Concrete, American Concrete Institute, Farmington Hills, MI, 2016, 76 pp.

About Master Builders Solutions

Master Builders Solutions is a leading global manufacturer of concrete admixtures, as well as other sustainable solutions for the construction industry, focussed on delivering its vision: **Inspiring people to build better.** Master Builders Solutions provides value-added technology and market-leading R&D capabilities to improve the performance of

construction materials and to enable the reduction of CO2 emissions in the production of concrete. Founded in 1909, Master Builders Solutions has ca. 1600 employees operating 35 production sites globally, supporting their customers in mastering their building challenges of today – for a decarbonised future.

Master Builders Solutions Admixtures US, LLC

23700 Chagrin Boulevard
Beachwood, OH 44122 USA
(800) 628-9990

master-builders-solutions.com/en-us
admixtures@masterbuilders.com

Master Builders Solutions Canada, Inc

1800 Clark Boulevard
Brampton, Ontario L6T 4M7 CANADA
(289) 360-1300

