Cement and Concrete Research 41 (2011) 263–269

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Physical and microstructural aspects of iron sulfide degradation in concrete

Thomas Schmidt [a,c,*], Andreas Leemann [b], Emanuel Gallucci [a], Karen Scrivener [a]

[a] EPFL, Swiss Federal Institute of Technology, Laboratory of Construction Materials, 1015 Lausanne, Switzerland
[b] Empa, Swiss Federal Laboratories for Material Testing and Research, 8600 Dübendorf, Switzerland
[c] Holcim (Schweiz) AG, Product development / -management, 5303 Würenlingen, Switzerland

ARTICLE INFO

Article history:
Received 16 April 2010
Accepted 17 November 2010

Keywords:
Concrete
Durability
Iron sulfide
Pyrite
Aggregates

ABSTRACT

The microstructural aspects of iron sulfide degradation in dam concrete were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) in both dam concrete samples and laboratory concrete. The results show that iron sulfide inclusions with a diameter of a few micrometers in the aggregates are reactive and appear to generate expansion first in the aggregates and consequently in the cement paste. The expansion from the iron sulfides is a consequence of the increase in volume of the reaction products formed. The types of iron sulfide present in the aggregate, mainly pyrrhotite (FeS) and pyrite (FeS_2), show similar reaction behavior in the aggregates. The released sulfate can lead to a secondary ettringite formation in the concrete matrix, but the degradation associated with this appears to be minor. The reaction of the iron sulfides was found to be very slow even when laboratory samples were exposed to elevated temperatures.

1. Introduction

Iron sulfides are common minor constituents in many rock types. They have been implicated in causing damage in concrete due to expansion [1]. It is usually assumed that oxidation of the iron sulfide leads to the release of sulfate ions causing internal sulfate attack in the concrete with expansive ettringite formation [2–5]. However, the microstructural aspects of this process have not been examined in detail.

The oxidation of iron sulfides like ironmonosulfide (FeS), pyrrhotite, and irondisulfide (FeS_2), pyrite, in concrete structures is a complex process that involves a sequence of different chemical reactions [6]. In the presence of oxygen and moisture, iron sulfides are unstable and oxidize to form iron oxides as shown by reactions 1 and 2:

$$2FeS + 2H_2O + 4.5O_2 \rightarrow Fe_2O_3 + 2H_2SO_4 \quad (1)$$

$$2FeS_2 + 4H_2O + 7.5O_2 \rightarrow Fe_2O_3 + 4H_2SO_4 \quad (2)$$

These reactions release sulfuric acid, which may go on to react with the cement paste and the iron oxides formed may also form hydroxides in the moist environment of the concrete.

Some research has been done on the factors affecting solubility as well as the nature of the intermediate and final reaction products of iron sulfides [7–10]. It was found that increasing concentration of molecular oxygen, higher alkalinity (pH), and smaller particle sizes accelerate the degradation of iron sulfides. The reaction kinetics of iron sulfides were found to depend on different parameters of the concrete such as porosity, inhomogeneity, and moisture conditions [7,11]. The solubility of the iron sulfide minerals was found to be about four times higher for FeS than FeS_2 [12,13].

The present study focuses on the microstructural aspects of concrete degradation due to iron sulfides inclusions in aggregates. This was studied in concrete cored from a dam and in concrete prepared from similar aggregates and stored in water bath at 60 °C for 5 years. The study indicates that the oxidation process of the iron sulfide causes cracking directly within the aggregates. The formation of secondary ettringite in the cement paste component was observed, but this did not seem to be a major cause of degradation.

2. Materials and methods

2.1. Field and laboratory samples

The study was carried out on two different concretes, concrete from a dam and concrete prepared from similar aggregates in the laboratory. The dam has a length of 290 m and an overall height of 36 m. Since the construction of the dam in the beginning of the 1970s, it has been monitored continuously for more than 40 years. It was observed that since the early 1980s, the concrete is steadily expanding. The upstream displacement of the dam in 1998 is 20 mm at the top and about 5 mm in the middle gallery (Fig. 1). Today the respective values are 45 and 10 mm. The overall expansion in the upper part of the dam is estimated to be 0.025%. However, it should be noted that the measured expansion only accounts for two

* Corresponding author. EPFL, Swiss Federal Institute of Technology, Laboratory of Construction Materials, 1015 Lausanne, Switzerland. Tel.: +41 58 850 57 80; fax: +41 58 850 55 71.
E-mail address: thomas.schmidt@holcim.com (T. Schmidt).

0008-8846/$ – see front matter
doi:10.1016/j.cemconres.2010.11.011