



Degradation of cement-based materials by various organic acids in agro-industrial waste-waters

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ABSTRACT

The paper analyses the mechanisms of the degradation of cementitious materials by three organic acids: oxalic, citric and tartaric acids, and evaluates their relative aggressiveness compared to that of acetic acid. These acids have different chemical characteristics in terms of poly-acidity and chemical and physical properties of their calcium salts. The aim was to highlight the links between these properties and the aggressiveness of each acid toward concrete. Degradation mechanisms and kinetics were investigated (using EPMA, XRD and SEM) on cement paste specimens immersed in acid solutions for one year.

The results showed that oxalic acid was not aggressive to the matrix. Citric acid caused the highest kinetics and severe degradations in the paste. Tartaric acid attack developed in two stages: no visible degradation was observed in the first weeks and then damage occurred, the kinetics remaining moderate. Acetic acid had intermediate aggressiveness.

It was confirmed that the solubility of the calcium salts was a major parameter of aggressiveness. It also appeared that, even if salts precipitated, they were not necessarily protective, the protection being correlated with the salt's molar volume. Moreover, poly-acidity seemed, in some cases, to increase the aggressiveness of the acid.

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1. Introduction

Concrete in agro-industrial environments may suffer severe degradation, notably linked with attack by waste waters [1–3] such as liquid manure and silage juice produced by stock-rearing activities, whey and white and green waters generated by the dairy industries, or molasses and vinasses from distilleries and the sugar industry. These waste waters contain a broad range of organic acids, which are responsible for acid attacks on concrete [1,4]. The acids can be found in the plants or fruits themselves, or they can come from the metabolism of the microorganisms found in the effluents.

Table 1 gives the composition in acids and the pH of various effluents that are chemically aggressive for concrete.

Acetic and propionic acids and other volatile fatty acids (VFA are carboxylic acids with fewer than 5 carbon atoms), and also lactic, oxalic, succinic and tartaric acids, are found in the effluents. The total concentration may reach several hundreds of millimoles per litre. The resulting pH is between 4 and 7. VFA and lactic acid are found in most effluents. In vinasses and molasses, tartaric, succinic, oxalic, malic, aconitic and fumaric acids are also found. The concentrations of acids in the effluents depend on many factors, among which are the fruit variety, the weather (temperature, humidity), the dilution rate and conditions of storage of the effluents, the way the animals are fed, etc.

Despite containing the highest concentrations of acids, liquid manure is the least aggressive of the effluents listed because of its high pH linked to the presence of the acid–base pair $\text{NH}_4^+/\text{NH}_3$.

Attacks by silage juice and liquid manure have been reported in the literature [2,4,15] but attack by molasses or vinasses have been little explored, if at all.

The development of concretes that perform well in such environments requires an understanding of the interaction mechanisms between the acid and the cement-based matrix. These acids have very varied chemical characteristics, which lead to significantly different aggressiveness to concrete [16,17]. Moreover, waste waters generally contain several acids and the resulting attack of the mixture of acids is not necessarily the superposition of the alteration caused by each acid taken separately [4,18,19]. The problem is thus complex and, to adequately understand the phenomenon, each acid should be considered individually with regard to its properties before mixes of acids are studied.

From a general point of view, organic acids, which are weak acids, partly dissociate in water and react with hydrated (notably C–S–H and CH) and anhydrous phases of the cement paste to give mainly calcium salts or complexes. The degradation mechanisms are linked with the characteristics of the acids and their associated salts and complexes. The dissociation constant of an acid and the solubility of a salt are known to directly influence how aggressive the acid is [16–18]. When the calcium salt is soluble (case of acetic and lactic acids), the degradation mechanisms are comparable to those induced by strong acids with soluble calcium salts such as nitric and hydrochloric acids

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