Science of the Total Environment 468–469 (2014) 358–367

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Is the transformation/dissolution protocol suitable for ecotoxicity assessments of inorganic substances such as silica fume?

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HIGHLIGHTS

- The transformation/dissolution potential of silica fume has been assessed.
- The T/D data has been compared with ecotoxicity hazard validation tests.
- Use of 7 day T/D test data alone would have resulted in false hazard classification.
- A suggestion of water solubility descriptors has been proposed.

ARTICLE INFO

Article history:
Received 11 June 2013
Received in revised form 13 August 2013
Accepted 13 August 2013
Available online 14 September 2013

Editor: Mark Hanson

Keywords:
Silica fume
Transformation/dissolution
Ecotoxicity
Solubility

ABSTRACT

Performing ecotoxicity tests on poorly water soluble substances and in particular metals, metalloids, and metal oxides such as silica fume, can be problematic. Such substances may not be directly toxic to aquatic organisms but often have high concentrations of impurities present, due to production processes, which may result in ecotoxicological effects. This combined with possibly testing above the limit of solubility further exacerbates the interpretation of ecotoxicity test results. One approach to overcome this is to perform a transformation/dissolution (T/D) test to determine the quantities of elemental impurities which will consequently be in solution. These data can subsequently be compared to existing data to determine if there is likely to be an effect on aquatic organisms. This paper highlights research into determining the T/D potential of 2 different grades of amorphous silica fume (low and high grade purity) with complementary chronic ecotoxicity tests of the 2 substances to validate this approach. The low grade silica fume test substance was identified in the T/D assessments as being of concern for the potential to cause acute toxicity to aquatic organisms and had levels of impurities (e.g. Pb and Zn) in the solutions which exceeded the effect limits identified in the open literature. Consequently, silica fume would be hazard classified as acute 2 according to regulatory classification schemes. However, the results of the ecotoxicity hazard validation assessments in a *Daphnia magna* reproduction test and the sediment dwelling organism *Chironomus riparius* indicated that low and high grade silica fumes are not acutely or chronically toxic up to and including an initial loading concentration of 100 mg/L and 1000 mg/kg respectively. Hence, using the T/D test data alone may have resulted in a false hazard classification of silica fume (low grade).

1. Introduction

According to Lutgens and Tarbuck (2000), over 90% of the Earth's crust is composed of silicate minerals, meaning that silicon is the second most abundant element, after oxygen (approximately 28% by mass). Consequently, SiO_2 is the most abundant compound within the Earth's crust (Heiserman, 1992). Silica fume (CAS no. 69012-64-2) is an amorphous, non-crystalline, polymorph of SiO_2. It is also known as condensed silica fume or microsilica and is collected as a by-product from silicon and ferro-alloy production in electric arc furnaces in quantities of around 1 million tonnes per year (Friede and Fidjestøl, 2011). Silica fume particles exhibit a perfectly spherical particle shape (Fig. 1) and are extremely small with a particle size between 20 nm and 1 μm and a d50 of approximately 150 nm (Friede and Fidjestøl, 2011). It consequently has a high BET surface area, typically between 15 and 30 m^2/g. Due to its unique physico-chemical properties, amorphous silica fume is a highly reactive pozzolanic material (i.e. a siliceous material that reacts with calcium hydroxide ($Ca(OH)_2$) to form cementicious phases). Hence, the main field of application of silica fume is the production of high-strength concrete, as well as sulphate and sea water resistant concrete.

Due to the choice of raw materials and the nature of the production of silicon and ferrosilicon alloys, silica fume is not synthetically pure

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http://dx.doi.org/10.1016/j.scitotenv.2013.08.035

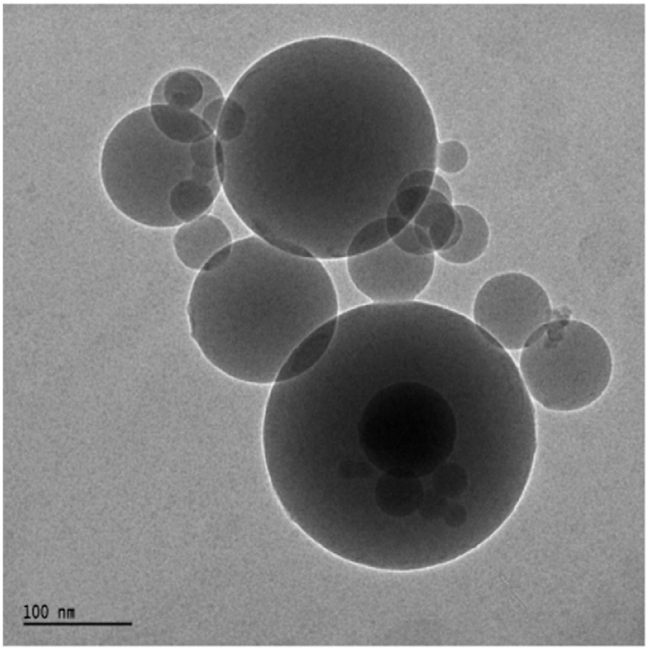

Fig. 1. Transmission electron microscope micrograph of a silica fume agglomerate. Philips CM 30, FEG, 300 kV, magnification ×32000.

SiO_2 but contains a number of impurities, such as inorganic carbon, alkali and alkaline earth metals, iron and traces of other metals such as lead and chromium. Due to these additional impurities there may be a possibility that ecotoxicological effects could be seen in the aquatic environment which are not due to the SiO_2 in the silica fume. Furthermore, silica fume has a low solubility level and performing ecotoxicological assessments with such poorly water soluble substances can be problematic. Recent work to determine protocols for the ecotoxicity testing of poorly water soluble mixtures have been reported (Gade et al., 2012) however, these have involved mainly organic constituents and not inorganic substances, such as silica fume. In addition, performing ecotoxicity tests on substances at concentrations exceeding the water solubility limit (i.e. using a higher initial loading rate to obtain higher levels of dissolved Si in the water) can result in impurities (e.g. Cu, Pb and Zn) that may dissolve at a different rate to the Si. This will result in an increased aqueous concentration of impurities which may cause ecotoxicological effects. Additional considerations to testing with poorly water soluble substances are further confounded by the fact that the definition of what actually constitutes a poorly water soluble substance is ambiguous. For example, the Organisation for Economic Cooperation and Development (OECD) guidance document number 23 indicates that a substance with a water solubility of <100 mg/L is considered to be poorly water soluble. In contrast, the Registration, Evaluation, Authorisation, and restriction of Chemicals (REACH Regulation (EC) No 1907/2006) endpoint specific guidance document (Chapter R.7.B, Table R.7.8-3) indicates that poorly water soluble substances are typically <1 mg/L. In addition, Annex 9 of the UN Global Harmonised System of classification and labelling of chemicals (GHS, 2011a) indicates that there appears to be little (consistent) guidance about descriptive terms regarding solubility ranges. Hence, there is a need for clear definitions on water solubility descriptors.

Silica fume has a reported solubility of between 0.75 and 2.6 mg/L (high and low grade respectively) (OECD 105 test guideline) and is considered to be a substance with a low solubility level (Herting et al., 2010). For sparingly soluble metals and metalloid substances such as silica fume, environmental hazard assessments can be performed using data on particle dissolution and metal release by using the OECD Transformation/Dissolution (T/D) protocol (OECD, 2001) and according to Annex 10 of the GHS (2011b). The principle of the T/D test is to determine the concentration of metal elements that are released from poorly water soluble substances and is defined as "the rate and extent to which metals and sparingly soluble metal compounds can produce soluble bioavailable ionic and other metal-bearing species in aqueous media under a set of standard laboratory conditions representative of those generally occurring in the environment" (OECD, 2001). These T/D data can then be compared with data that are already available for each of the elements to determine if the concentration released is above the concentration expected to cause an effect in the aquatic environment. These data can subsequently be used to hazard classify substances based on the hazard classification system in Annex 9 of the GHS (2011a).

The T/D test protocol has been successfully used on other metal alloys (Skeaff et al., 2008; Hedberg and Odnevall Wallinder, 2012), but previous T/D tests on silica fume (and other Si based alloys) have only been performed using the 24 hour T/D screening test (Herting et al., 2009a,b). Due to the identification of elemental impurities (e.g. Cu, Pb and Zn) in the 24 hour T/D screening test which may cause effects to aquatic organisms (Lillicrap, 2010), a full T/D assessment has subsequently been performed on silica fume to further substantiate whether either grade of silica fume require environmental hazard classification (Lillicrap et al., 2011). The T/D tests were performed for a period of 7 and 28 days, representing potential acute and chronic effects respectively. Subsequently the T/D data was compared with existing ecotoxicity data for the different elements to determine if either substance should be hazard classified.

An important consideration with assessing the T/D data is the measurement of the actual bioavailable concentration of potential elemental impurities present in the solutions. To this end, the diffusive gradients in a thin film (DGT) technique can be used to estimate concentrations of metals in the free ionic form or forming labile complexes in solution (Davison and Zhang, 1994). The DGT technique is based on a simple device that enables the accumulation of dissolved trace metal species on a chelating resin, following diffusion through a well-defined and permeable hydrogel layer. The device is deployed for a known period of time and the mass of metal on the resin layer is quantitatively measured. The concentration in solution can then be calculated from known diffusion coefficients in the hydrogel layer (DGT research handbook) if the temperature is known. Any dissolved species for which there is a selective binding agent can be measured. For trace metals, the standard version of DGT can be employed to sample metals such as Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn however, many more metals are also possible, including rare earth elements (Garmo et al., 2003).

In addition to the T/D tests and to fulfil potential data requirements of the REACH regulation, a chronic ecotoxicity test for both grades of silica fume on the freshwater crustacean *Daphnia magna* was also performed. Furthermore, due to the physical nature of silica fume and its likelihood of partitioning into the sediment phase of aquatic systems, a chronic ecotoxicity test on the sediment dwelling organism *Chironomus riparius* was also carried out. These data were then compared to the T/D data to further validate the requirement for additional ecotoxicity testing for poorly water soluble substances assessed using the T/D protocol. This paper also highlights some of the challenges involved with assessing potential effects of poorly water soluble metals and metalloids and suggests potentially appropriate approaches to overcome these problems. Furthermore, a proposal for defining water solubility descriptors has been developed.

2. Materials and methods

2.1. Test substances

Silica fumes (CAS number 69012-64-2) of low and high grades (purity of 83.8% SiO_2 and 96.4% SiO_2 respectively) were obtained from Elkem AS, Silicon Materials, Kristiansand, Norway. According to the certificate of analysis supplied by Elkem AS, the silica fume (low grade)