



# Self-heating of dried industrial tannery wastewater sludge induced by pyrophoric iron sulfides formation



R. Bertani<sup>a,\*</sup>, A. Biasin<sup>a</sup>, P. Canu<sup>a</sup>, M. Della Zassa<sup>a</sup>, D. Refosco<sup>b</sup>, F. Simionato<sup>a</sup>, M. Zerlotti<sup>b</sup>

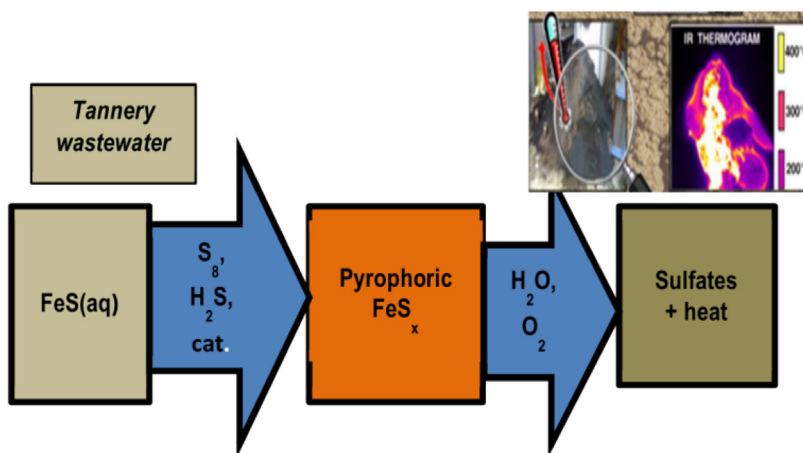
<sup>a</sup> Department of Industrial Engineering, University of Padua, Via Marzolo, 9, 35131 Padova, Italy

<sup>b</sup> Acque del Chiampo, SpA, Via Ferraretta, 20, 36071 Arzignano (VI), Italy

## HIGHLIGHTS

- Dramatic self-heating until self-combustion tannery sludge.
- Pyrophoric iron sulfides formation in tannery sludge drying under suboxic atmosphere.
- In the sludge, the chemistry of iron sulfides in marine systems is reproduced.
- Lab-scale preparation of reactive dried sludge.
- Sludge characterization by physical and chemical analytical techniques.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 7 July 2015

Received in revised form

16 November 2015

Accepted 19 November 2015

Available online 23 November 2015

### Keywords:

Tannery sludge

Tannery wastewater

Self-heating

Pyrophoric iron sulfides

## ABSTRACT

Similarly to many powders of solids, dried sludge originated from tannery wastewater may result in a self-heating process, under given circumstances. In most cases, it causes a moderate heating (reaching 70–90°C), but larger, off-design residence times in the drier, in a suboxic atmosphere, extremely reactive solids can be produced. Tannery waste contains several chemicals that mostly end up in the wastewater treatment sludge. Unexpected and uncontrolled self heating could lead to a combustion and even to environmental problems. Elaborating on previous studies, with the addition of several analytical determinations, before and after the self-heating, we attempted to formulate a mechanism for the onset of heating. We demonstrated that the system Fe/S/O has been involved in the process. We proved that the formation of small quantities of pyrophoric iron sulfides is the key. They are converted to sulfates by reaction with water and oxygen with exothermic processes. The pyrite/pyrrhotite production depends on the sludge drying process. The oxidation of sulfides to oxides and sulfates through exothermic steps, reasonably catalyzed by metals in the sludge, occurs preferentially in a moist environment. The mechanism has been proved by reproducing in the laboratory prolonged heating under anoxic/suboxic atmosphere.

© 2015 Elsevier B.V. All rights reserved.

\* Corresponding author. Fax: +39 049 8275525.

E-mail address: [roberta.bertani@unipd.it](mailto:roberta.bertani@unipd.it) (R. Bertani).

## 1. Introduction

The occurrence of spontaneous self-heating of powders, until self-ignition, is well known [1]. These include coal [2], metals [3], solid biomass [4] (for examples wood dust and pellet [5]): wastes are common in the latter category [6].

In industrial processes using large volume of organic materials two sources of heat-generation are usually considered: a low temperature process involving the growth and respiration of microorganisms and a high temperature process due to oxidation of organic matter [7]. Typically biological activity can determine temperatures of the order 70–90 °C that can prelude to self-ignition [8]. Management of the risk of dust self-heating and ignition (until possible explosion) is a challenging task, since the complexity of the process involved is not completely understood. The risk is real, in particular, for landfills [9], silos [10] and stored food waste to be used for recycling [11].

The influence of different parameters (i.e. amount of material, composition, volatile and inert matter content, particle size, pH, moisture content, shrinkage, porosity, oxygen concentration and diffusion, presence of catalysts) on self-heating and spontaneous combustion has been investigated [12]. European Standards (i.e. minimum ignition energy, MIE; minimum ignition temperature, MIT; minimum explosive concentration, MEC; limiting oxygen concentration, LOC) have been indicated to evaluate thermal susceptibility, ignition sensibility and explosion severity of different dust samples [6]. Mathematical models, based on thermodynamic and transport properties, to simulate the processes and identify more critical parameters have been also developed [13].

To design the prevention and protection measurements needed in all industrial plants a risk assessment is indispensable. Several researchers have demonstrated that it is essential to characterize the sludge to have a complete scenario of the hazard [14].

Here, we study the onset of spontaneous heating in dried sludge originated from primary and biological treatment of both municipal and industrial wastewater, the latter largely dominant (approx 90% total organic carbon), mainly originated from tanneries [15]. The study aims at understanding the chemistry behind the spontaneous heating, eventually suggesting prevention measures. Here we discuss chemical paths leading to heat development, focusing on the solids characterization investigated by several analytical techniques.

## 2. Materials and Methods

### 2.1. Materials

The origin and sample labeling is reported in Fig. 1. The original solid waste (dry sludge, samples **A** and **B**) was always obtained

in the industrial process [15]. Sludge was obtained by collecting both raw wastewater and floatation with subsequently dewatering and thermal drying. Sludge in the form of powder with granules of approx. 2 mm mean size, with 85–92% dry solid content and 0.7 kg/L apparent density was usually stored in big-bags then moved to a dedicated landfill. The average composition (determined by inductively coupled plasma, ICP) was characterized by high level of chromium, iron and sulfur [15].

To obtain sample **C** the original solid (sample **A**) has been reprocessed in a stainless steel autoclave. 20 g of sludge **A** have been charged in a closed autoclave with internal volume of 70 mL. The sludge **A** has been heated at 1 °C/min to 300 °C, and maintained for 30 min. The solids was exposed to the air initially present in the reactor and the evolved products, allowed to escape through a hydraulic seal. The final material was named Sample **C**.

### 2.2. Analytical techniques

The composition of samples is quite complex, due to the heterogeneity (and seasonality) of the original wastewater. The sludge **A** is routinely analyzed at the plant, before disposal, to comply with legal requirements to be landfilled. In particular total chromium has been determined by atomic absorption and Cr(VI) according to the CNR IRSA Q64 3 1986 method by using Atomic Absorption after a selective coordination with ammonium pyrrolidone dithiocarbamate. However, such analyses are not specific enough to identify a chemical route leading to self-heating. Sludge microstructure and composition before and after the self-heating process have been studied through several analytical techniques. Combined differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TGAQ 5000 thermogravimeter analyzer, TA Instrument, under air atmosphere. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet spectrophotometer Avatar 320 as KBr pellets. Powder X-ray diffraction (XRD) analyses of the samples were carried out with a Philips powder diffractometer X'Pert MPD using PW3123/00 curved Cu-filtered Cu-K $\alpha$  radiation at a generator voltage of 40 kV and a generator current of 30 mA. The diffractograms were scanned in the 2 $\theta$  range from 1.5° to 30° at 0.01°/s rate in continuous scan. The microanalyses and morphologies of the samples have been studied by means of ESEM (environmental scanning electron microscope, Philips XL 30-X-ray fluorescence, XRF embedded). The surface composition of the samples was investigated by XPS. The analyses were performed on a PerkinElmer  $\Phi$  5600-ci spectrometer using non-monochromatized Al-K $\alpha$  radiation (1486.6 eV). The working pressure was  $<5 \cdot 10^{-8}$  Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f<sub>7/2</sub> line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.15 eV. The reported BEs were corrected for the charging effects, assigning to the C1s line of adventitious carbon a value of 284.8 eV. Survey scans were obtained in the 0–1200 eV range. Detailed scans were recorded for the C1s, O1s, Si2p, N1s, S2p, Fe2p, Cr2p and Ca2p regions. The analysis involved Shirley-type background subtraction, non-linear least-squares curve fitting, adopting Gaussian–Lorentzian peak shapes and peak area determination by integration. The atomic compositions were then evaluated using sensitivity factors supplied by PerkinElmer, taking into account the geometric configuration of the apparatus. The sample powders were introduced directly, by a fast entry lock system, into the XPS analytical chamber. Continuous Wave (CW) electron-paramagnetic resonance (EPR) spectra at X-band were recorded using a Bruker ER200D spectrometer equipped with a standard rectangular cavity (ER 4102ST). Experiments were carried out at 298 and 180 K using a Bruker VT5113 temperature controller. The W-band CW-EPR spectra were recorded using a

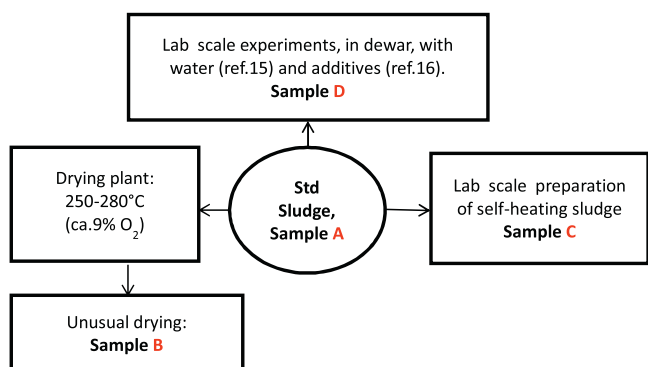


Fig. 1. Flow diagram of the sludge treatment, with sample identification.

Download English Version:

<https://daneshyari.com/en/article/575526>

Download Persian Version:

<https://daneshyari.com/article/575526>

[Daneshyari.com](https://daneshyari.com)