Waste Management 34 (2014) 817–824

Contents lists available at ScienceDirect

Waste Management

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

On the understanding and control of the spontaneous heating of dried tannery wastewater sludge

A. Biasin [a], M. Della Zassa [a], M. Zerlottin [b], D. Refosco [b], R. Bertani [a], P. Canu [a,*]

[a] Dept. of Industrial Engineering, University of Padua, Via Gradenigo, 5/a, 35131 Padova, Italy
[b] Acque del Chiampo, SpA, Via Ferraretta, 20, 36071 Arzignano (Vi), Italy

ARTICLE INFO

Article history:
Received 8 September 2013
Accepted 31 December 2013
Available online 29 January 2014

Keywords:
Spontaneous heating
Dried sludge
Self-heating
Autoignition
Iron/sulphur
Tannery waste

ABSTRACT

We studied the spontaneous heating of dried sludge produced by treating wastewater mainly originating from tanneries. Heating up to burning has been observed in the presence of air and moisture, starting at ambient temperature. To understand and prevent the process we combined chemical and morphological analyses (ESEM) with thermal activity monitoring in insulated vessels. Selective additions of chemicals, either to amplify or depress the reactivity, have been used to investigate and identify both the chemical mechanism causing the sludge self-heating, and a prevention or a mitigation strategy. FeS additions accelerate the onset of reactivity, while S sustains it over time. On the contrary, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, $FeCl_2$, EDTA, NaClO can limit, up to completely preventing, the exothermic activity. All the experimental evidences show that the reactions supporting the dried sludge self-heating involve the Fe/S/O system. The total suppression of the reactivity requires amounts of additives that are industrially incompatible with waste reduction and economics. The best prevention requires reduction or removal of S and Fe from the dried solid matrix.

1. Introduction

After the occurrence of unusual temperature in a dedicated landfill for exclusive disposal of dried sludge from tannery wastewater treatment, an extensive investigation to evaluate the hazard, the self-heating causes and the prevention strategies has been carried out. We already reported (Zerlottin et al., 2013) a large scale experimental study, based on 1 m^3 big-bags, where we deterministically reproduced the self-heating processes, observing two distinct behaviors, depending on the drying operations. Either the sludge mass increases its temperature up to a maximum of approx. 90 °C before cooling or an unbounded temperature rise leads to self-combustion, without any flame. The second case is extremely critical for safety and pollution (Nammari et al., 2004), but we clearly proved that it occurs only after an uncontrolled drying operation. Yet, some heating is always observed, but in most cases it is weak enough to independently extinguish in a few days, depending on the heat exchange rate of the sludge mass and its aeration. The sequence of a faint heating that may trigger total combustion has been reported by many authors, on wastewater sludge (Poffet et al., 2008), as wells as other solid wastes (Moqbel et al., 2010; Hogland and Marques, 2007, Hogland et al., 2009; Buggeln and Rynk, 2002; Shimizu et al., 2009), and solid fuels, typically coal (Carras and Young, 2004; Nelson and Chen, 2007; Ribeiro et al., 2010; Phillips et al., 2011; Day, 2000).

We devised a procedure (Della Zassa et al., 2013) to reproduce the initial self-heating process at the laboratory scale, to manipulate either the solids or its environment, aiming at investigating the mechanism. So far we reported the enhancing (or damping) effect of aeration, moisture content (also by addition of water) particle size, bed and particle porosity and biological activity (Della Zassa et al., 2013). Apparently, fermentation is rather marginal in the heating process (Della Zassa et al., 2013; Li et al., 2006); a chemical route is clearly prevailing, as confirmed by spontaneous heating and combustion of solids that have little or no putrescible components, such as coals (Carras and Young, 2004; Nelson and Chen, 2007; Ribeiro et al., 2010; Phillips et al., 2011; Day, 2000), refuse derived fuel (RDF) (Yasuhara et al., 2010; Fu et al., 2005; Li et al., 2008) and refuse plastic/paper fuel (RPF) (Li et al., 2009). In most of these cases, the inorganic components are deemed responsible of the self-heating potential (Sujanti and Zhang, 1999), in addition to moisture that is always a key factor.

Here we aim at better understanding the chemical mechanism that supports the self-heating process, beyond simple thermal monitoring, to include chemical and morphological analysis of the solids, mainly performed by ESEM–EDS technique, as well as discussing the effect of chemical additives expected to inhibit or delay the self-heating process. Finally, the process understanding's goal is the identification of prevention policies, including

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* Corresponding author. Tel.: +39 049 8275463; fax: +39 049 8275461.
E-mail address: paolo.canu@unipd.it (P. Canu).

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http://dx.doi.org/10.1016/j.wasman.2013.12.023

modifications of the sludge production process, as well as remediation actions, in case of uncontrolled heating in large storages.

2. Materials and methods

2.1. Materials

All tests used dried sludge as produced by the same industrial drying plant (Zerlottin et al., 2013), which processes sludge resulting from the treatment of wastewater of a large tannery district and a minor amount (approx. 10%) of municipal sewage wastewater. Dried sludge appears as a coarse powder, made of brittle granules with an average particle size of 2 mm and a residual moisture content varying in the 8–15 wt% range. It is a complex solid matrix that is affected both by the large quantity (and variety) of chemicals used in the tanning industry and by the additives introduced during the water treatment process. The heterogeneity (and seasonality) of the original wastewater contributes to this complexity as well. The dried sludge is routinely analyzed to comply with legal requirements in order to be landfilled, but the analyses typically used are not specific enough to identify the chemical route leading to self-heating. Proximate analysis reports, beside moisture (by drying at 105 °C for 24 h), a large fraction of volatiles, leaving residual solids for approx. 25–30% of the initial weight (after incineration at 600 °C for 4 h). The elemental analysis has been already reported (Della Zassa et al., 2013).

Milli-Q water (18.0 $M\Omega\ cm^{-1}$) generated from a NANOpure Diamond purifying system was used for all experiments. $Ca(OH)_2$, $CaCO_3$, Na_2CO_3, $NaHCO_3$, S, FeS, $FeCl_2$, NaClO and EDTA (Ethylenediaminetetraacetic acid) were used as additive in dedicated experiments. All were used as purchased (Sigma–Aldrich).

2.2. Batch experiments

The dried sludge spontaneous heating always occurs immediately downstream of the drying process, as previously described (Zerlottin et al., 2013) but usually the heating rate is rather weak. Factors like the heat exchange rate of the sludge mass and its aeration affect the rate and intensity of self-heating. Simple techniques to bring the dried sludge to the laboratory preserving its reactivity have been adopted, by keeping the sludge samples under vacuum (Della Zassa et al., 2013). At the laboratory scale, the reactivity of the sludge has been determined by batch experiments in thermally insulated vessels (adiabatic tests), where temperature is continuously monitored over long periods of time (Della Zassa et al., 2013). Typically, a reference amount of dried sludge (250 g) was loaded inside an insulated flask (sometimes called *Dewar*) and the core temperature of the sample mass was monitored using K type thermocouples, approx. at its center. Data were continuously logged by a computer, through commercial data acquisition boards (Measurement Computing) The dried sludge has been studied either alone or mixed with additives, always using the same reference amount of dried sludge and a water quantity of 50% of the initial sludge sample's mass, approaching a final moisture content of approx. 40 wt% (unless specified differently). Water addition and aeration (the upper surfaces of the insulated vessels were always kept open to air) are requirements to trigger the spontaneous heating, although their role in the mechanism was not clear, so far. Additives that have been tested include $Ca(OH)_2$, $CaCO_3$, Na_2CO_3, $NaHCO_3$, S, FeS, $FeCl_2$, NaClO and EDTA (Ethylenediaminetetraacetic acid). Because the process of self-heating is triggered by water, we tried to formulate all the mixtures of sludge and additives as powders, although the contact is less effective. The water content was then determined by our intentional addition. Additive amounts vary between 5% and 30% by weight of the initial sludge. That was the case of all the additives, independently of the solubility, except for NaClO and EDTA that have been added as water solutions by spraying, over the sludge sample spread on a horizontal surface as a thin layer.

In the case of solids mixtures, water was always added by spraying right before loading the mixture in the insulated vessel. It is noteworthy that other addition procedures can be envisaged (Sujanti and Zhang, 1999), including deionized water or acid-washing to remove most of the inorganic components, soaking the solids in the solution carrying the additives, followed by filtering and drying of the treated solids. We avoided these alternative procedures to prevent affecting the sample structure, both chemically and physically, as well as its reactivity.

A large number of tests have been carried out, lasting between 2 weeks and a few months, spanning a period of almost 1 year, notwithstanding some parallelization of the tests. The drying plant yields a product with features varying at high- (days) and low- (seasonal) frequency. Accordingly, the properties of collected samples of dried sludge gradually vary in time, so that new batches must be periodically collected. For these reasons, (i) comparative tests have been carried out simultaneously, on the same batch of sludge and (ii) the untreated sludge behavior reported in different figures may slightly vary because it originates from different sampling batches.

2.3. Analytical methods

The main criteria to quantify the sludge thermal activity is always a time record of temperature. In addition, proximate analysis of the sludge has been carried out with conventional ovens and analytical balances. Solids residues have been analyzed for elemental composition by ICP (Perkin Elmer OES OPTIMA 7300 DV). Sludge microstructure and composition before and after the self-heating process have been studied by ESEM (environmental scanning electron microscope, Philips XL 30-EDS embedded) at 20–30 kV.

3. Results and discussion

3.1. ESEM analyses

Scanning electron microscopy turned out to be quite useful both for the local elemental composition and the morphology, although limited to a shallow surface layer. Elemental analysis is obtained on superficial spots of variable size by X-ray fluorescence emissions using an Energy Dispersive Spectrometer (EDS). The composition is averaged on the spot area; a careful selection is required.

Significant differences in the sludge samples, before and after the heat generation, have been observed. The elemental analyses averaged over a number of local surface spots of about 1 mm^2 are reported in Table 1. Results are fairly consistent with ICP measurements already reported (Della Zassa et al., 2013). Carbon and oxygen prevail, while nitrogen, chromium, sulfur, calcium and iron are the most relevant minor species.

The analysis of post-heating sludge reported in Table 1 was representative of an average result; slightly different composition might be observed depending on the intensity and extent of the self-heating phase. Still, we observe that the self-heating activity causes a decrease of carbon (approx. −10 wt%) and sulfur (approx. −40 wt%) while oxygen increases (approx. +10 wt%, it reflects the addition of water and the aeration).

A very peculiar feature is the presence in all the samples of dried sludge, before the heating activity, of regular orthorhombic bi-pyramidal crystals (Fu and Manthiram, 2012; Meyer, 1976), as