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SVM application in hazard assessment: Self-heating for sulfurized rust

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ABSTRACT

In order to assess the oxidation self-heating hazard of sulfurized rust, for particular ambient conditions in crude oil tanks, the support vector machine (SVM) technique is applied to predict the maximum temperature (T_{max}) of oxidation self-heating process. Five governing parameters are selected, i.e. the water content, mass of sulfurized rust, operating temperature, air flow rate and oxygen concentration in the respiratory/safety valve. The efficiency and validity of the SVM predictions are investigated in the case of two sets of data: more than 85 experiments performed in academic lab (China) and almost 17 additional results collected from existing literature. Two main steps are also discussed: the training process (on selected subsets of data) and prediction process (for the remaining subsets of data). It can be concluded that for both datasets the maximum temperature (T_{max}) values calculated by SVM technique were in good accordance with the experimental results, with relative errors smaller than 15% except for a few cases.

The SVM technique seems therefore to be relevant and very helpful for complex implicit processes such as chemical reactions, as it is the case of the oxidation of sulfurized rust in oil tanks. Furthermore, such predictive methods can be continuously be improved through additional experiments feedback (larger databases) and can then be of crucial help for monitoring and early warning of hazardous reactions.

1. Introduction

Self-heating caused by oxidation of sulfurized rust may generate disastrous situations due to fire and explosion in oil tanks. In Sinopec Group or China National Petroleum Corporation (CNPC), these initial accidents occur regularly (Zhao et al., 2011, 2007). Such events can also trigger secondary sequences and cascading accidents leading to domino effects. Actually, sulfurized rust formed on the inside-walls and respiratory/safety valve inner cavity of tanks reacts with hydrogen sulfide at low-temperature. It results in formation of sulfurized rust in the process of transportation and storage of crude oil (Walker et al., 1987; Dou et al., 2014), for instance.

In general, application of nitrogen blanketing technique to oil tank could protect the sulfurized rust on the inside-walls from oxidizing air. Nevertheless, the sulfurized rust in the inner cavity of respiratory/safety valve reacts with hydrogen sulfide and oxygen recurrently because of the oil delivery and reception as well as the big and small breath which gives more possibilities of self-heating (Qiao and Li, 2013). The oxidation self-heating process of sulfurized rust is susceptible to internal or external factors which comprise pH, water content, mass and constituents of sulfurized rust and operating temperature in oil tank, flammable gas volume fraction in ullage space, air flow rate through the respiratory/safety valve as well as flowing oxygen concentration from several studies (Walker et al., 1997, 1996, 1988; Li et al., 2005; Zhao et al., 2007; Li

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et al., 2011, 2006) and our previous experimental work. Furthermore, on the basis of the available literature (Yang and Wu, 2013; Wu et al., 2008; Hu et al., 2007), the temperature about 70 °C is not only the critical temperature at which chemical oxidation takes place but also the smoke point temperature at which SO_2 formation occurs. Therefore, it is thought that the 70 °C can be considered as the threshold temperature for the self-heating process. In this study, a temperature exceeding 70 °C is assumed to result in disastrous self-heating processes such as fire and explosions (Gabriele et al., 2011).

As the maximum temperature cannot be easily derived from the governing parameters values by explicit or theoretical relationship, several authors have investigated the oxidation process to determine the maximum temperatures based on experimental results (Walker et al., 1996; Zhao et al., 2007; Li et al., 2011, 2006). However, for the purpose of monitoring and early warning, the maximum temperatures of oxidation self-heating cannot be entirely covered by experiments. In quantitative risk assessment (QRA), support vector machine as a successful tool in machine leaning has been applied to resolve real-world engineering problems (Salcedo-Sanz et al., 2014).

It is worth to adopt such techniques in order to predict the maximum temperature that may be reached and the critical temperature that may trigger a first accident, which means that around 70 °C the spontaneous oxidation (pyrophoric) process works as an effective ignition source, i.e. the associated reaction energy coincides with the minimum ignition energy (MIE) in the case of sulfurized rust oxidation in oil tanks. The present study will focus on the prediction of maximum temperature and the critical temperature that may cause the first accident.

2. Experimental study and theoretical prediction of maximum temperature

2.1. Experiments and data collection

An experimental dataset consisting in a set of 85 groups has already been performed out at Nanjing Tech University (NJTech, China). They concern oxidation experiments carried out by means of the sulfurization & oxidation experimental apparatus shown on Fig. 1. The raw test samples were collected from the respiratory valve inner cavity of a crude oil tank in Jinling Petrochemical Company, whose main ingredient was rust. The particles diameter of the samples was ground to less than 250 μm. The sulfurization & oxidation experimental apparatus has four main parts:

- Part 1 for the gas supply section, which includes air cylinder, nitrogen cylinder, hydrogen sulfide cylinder and gas buffering & flow rate control;
- Part 2 for the measurement of air flow rate and humidification section, which contained a cone bottle with water and flow meter;
- Part 3 for the sulfurization & oxidation section, which involved a quartz tube twined with an electric heating tape and thermocouple;
- Part 4 was the tail gas buffering & absorption section, which comprises an empty cone bottle and the other with sodium hydroxide solution.

Prior to the sulfurization, each sample was placed in quartz tube which was fitted with glass wool plugs and taps at both ends. Then the gas route was connected, and the gas tightness of apparatus was checked. The air in apparatus was replaced by high purity nitrogen from N_2 cylinder with valves V2, V4, V7 open and other valves closed. The quartz tube was wrapped around with electric heating tape to keep the samples at 35 °C because the operating temperature of crude oil tank falls in the range from 25 °C to 35 °C. Afterwards, the sulfurization gas (made up of H_2S and N_2, V_{H2S}:V_{N2} = 2:3) passed through the water at the rate of 500 mL/min with valves V2, V3, V4, V5, V6, V9 open and other valves closed. This could make sure that the gas would be saturated by water with a given level in a similar condition as found in the crude oil tank. As none of other gases was produced in this process, the remainder of hydrogen sulfide was absorbed by NaOH solution. After 6 h sulfurization, the sulfurized rust was cooled to ambient temperature (20 °C).

After sulfurized rust preparation, the samples were used for the oxidation experiment. Before oxidation, the apparatus was filled with high purity nitrogen from N_2 cylinder with only valves V2, V4 and V7 open for 15 min till all the hydrogen sulfide had been exhausted. As samples reacting with mixed gas at different oxygen concentrations like the environmental conditions in the field, the valves V1, V2, V4, V5, V6 were open and other valves closed. In order to keep the samples with various water contents, the distance from gas inlet to water level in the conical flask was adjusted. Flow meter was used for controlling the gas flow rate. The different initial temperatures were regulated by the electric heating tape according to the experiment requirements. For the higher accuracy of experiments, oxidation of each sulfurized rust sample was repeated three times.

A set of 85 maximum temperatures values (T_{max}^{exp}) has been collected. They correspond to various water content, mass of sulfurized rust, operating temperature, air flow rate and oxygen

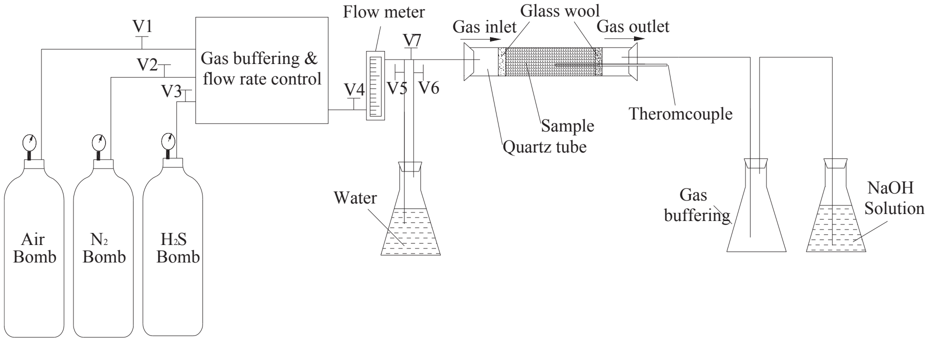

Fig. 1. Sulfurization & oxidation experimental apparatus.