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Detection of alkali emissions from alumina refining processes

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ABSTRACT

In this work, the feasibility of using pH based indicators as a microfluidic based online alkali detection method was evaluated. The indicators were tested towards sodium hydroxide solution through a flow cell followed by the measurement of their colour changes via UV–visible spectroscopy. Among the tested indicators, cresol Red and neutral red showed the largest usable sensitivity range towards solutions containing alkaline compounds. In order to test if the method would be suitable for operating in an alumina refinery atmosphere, each indicator was tested against weak bases and other species such as Na₂CO₃, NaHCO₃, MgNO₃ and NH₃. Under such situations, neutral red was found to be useful for sensing low NaOH concentrations (i.e. in the range of 10 to 50 μM in liquid, which is equivalent to 0.2 to 2 mg/m³ in air) and thus may be able to indicate when the concentration is approaching the alkali threshold (2 mg/m³). Similarly, cresol Red was also identified as a potential candidate to differentiate between low and higher threshold limits of equivalent NaOH concentrations (0.2 to 2 mg/m³) as it exhibited low susceptibility towards NaCl, NH₃ and NaHCO₃ contaminants.

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1. Introduction

Caustic (alkali) mist emissions from alumina refinery processes may pose occupational, health and safety as well as operational issues if not properly controlled (Leong and Connor, 2005). Alkali emissions may originate from a number of sources such as open tanks and purge equipment. The mist level depends greatly on the number of process parameters and mechanisms (i.e. splash filling, thermal currents in tanks, streams discharged from a pipe, tank temperatures, atomization), as well as the climatic conditions (e.g. wind speed and direction, rain, etc.) during normal operational activities (Leong, 2008). Currently, the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH) require alkali threshold limit values to be less than 2.0 mg_(alkali)/m³_(air). The NIOSH method (Method 7401) is primarily used for determining alkaline dust in air (Cassinelli, 1994), however, several other methods to detect alkali emissions have also been reported by Queensland Alumina Limited (QAL) and organisations such as NIOSH. These include filter pad methods, analytical methods based on titration, vibrational spectroscopy and proton induced X-ray emission (PIXE) analysis (Leong and Connor, 2005) (Korostynska et al., 2007; Leong, 2008; Lindfors

and Ivaska, 2002, 2005; Messer et al., 2005; Mohr and Wolfbeis, 1994), however these attempts have had very limited success. There is a need to develop a reliable and accurate alkali measurement system in order to assess the atmospheric alkali content so that appropriate operational procedures can be undertaken to rectify any potential issues. In this work, the feasibility of using pH indicators in a microfluidic based online alkali detection method is investigated.

2. Experimental

The methods described were designed to explore the use of pH indicators combined with spectroscopic methods for measuring alkali levels within aqueous filled traps. The required detection limit (in-line with NIOSH recommendations) is preferred to be in the 0.2 mg_(alkali)/m³_(air) range, which is 1/10th of the 2 mg_(alkali)/m³_(air) exposure limit or alarm triggering concentration. The majority of samples tested in this work were designed on the premise that a 25 L air sample containing between 0.2 to 2 mg_(NaOH)/m³_(air) would contain between 5 to 50 μg of NaOH equivalent alkali species for every 12.5 ml (equivalent to 10 to 100 μM) of a given aqueous trap solution.

2.1. Materials

Three different pH indicators (see Fig. 1) were investigated for NaOH sensing in the presence of chemical species which are found in alumina refinery environments and/or could potentially cause the system to

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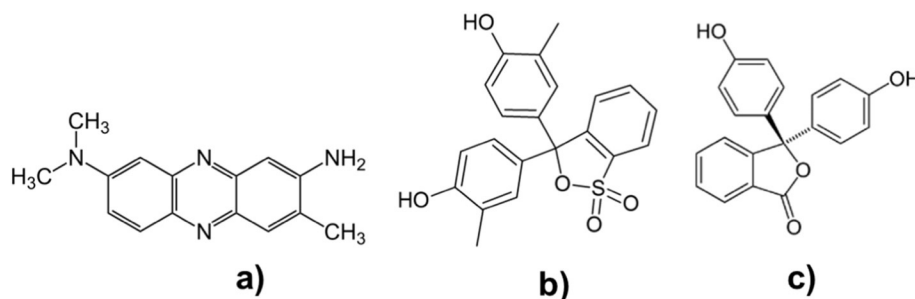


Fig. 1. Chemical structures of a) neutral Red, b) cresol Red and c) phenolphthalein.

report a false negative or false positive NaOH concentration. The intensity and colour change of the solution was monitored when mixing different alkaline solution with each dye.

The tables (Tables 1 to 3) given below summarise the set of chemicals that were used in the different type of experiments conducted during this research project.

2.2. pH probe measuring method

An initial study was undertaken to evaluate the feasibility of pH probes for NaOH detection. For the pH study of alkali and contaminant solutions, a pH 213 Hanna Instruments pH probe was calibrated with buffer solutions having pH of 4, 7 and 10. The readings were taken either immediately or 1 min after the probe had stabilized in the solution. The pH probe was rinsed using Milli-Q water in-between each measurement.

The solutions of interest are mainly alkaline – NaOH, NaHCO₃, NH₃, etc. – and can be related to the following acid/base formula (Eq. (1)):



Where A⁻ represents the base and HA the acid when dissociated in water.

In order to calculate the pH values of the alkali and contaminant solutions, the following formulas (Eqs. (2) & (3)) were used:

$$pH = -\log([H^+]) \quad (2)$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad (3)$$

where K_b is the base dissociation constant.

2.3. Alkali and contaminant detection

2.3.1. UV-visible spectrometer

In order to relate the colour intensity of the chosen pH indicators with the alkali concentration, a UV-visible continuous flow cell system was used. The pH indicator and alkali sample solutions were connected via PVC peristaltic pump tubes and pumped through fixed length Teflon tubes into a quartz cuvette. The mixture was then analyzed for their absorbance intensity using a Cary 60 Agilent UV-visible Spectrometer. For each experiment, the baseline was obtained using Milli-Q water as the blank sample along with the pH indicator being investigated.

Table 1
Indicators and solutions used for alkali detection and UV-vis signal optimisation.

Dye	Dye concentration (× 10 ⁻³ % w/v)	Solution	Concentration (μM)
Neutral Red	2.0, 2.9, 3.5, 4.1, 5.2	Sodium hydroxide	10–100
Cresol Red	0.5, 1.0, 1.5, 2.5, 3.5, 4.5		
Phenolphthalein	2.5, 17.5, 22.5, 37.5		

2.3.2. Flow cell setups

Fig. 2 shows the setup picture and corresponding flow diagram used to determine the performance of neutral Red, cresol Red and phenolphthalein pH indicators. The setup was mainly used to introduce various combinations of possible interfering chemical compounds. The system comprised of two multi-way valves which allowed for independently switching between the contaminants without affecting the NaOH sample flow. Each of the contaminant solutions was also set to a fixed concentration, thus improving the repeatability and minimising the chance of error when making solutions with multiple constituents. In all cases, the mixing of NaOH and the selected contaminant solution occurred downstream of the pump. The total flow was maintained at 5.8 ml/min in all stages of the experiments.

The flow rates for each channel/tube were determined through a basic calibration of the pump speed versus the total liquid dispensed from each tube. The pH indicator and alkali ratios were controlled using a 4-to-1 multi-way valve which was connected to a bank of NaOH solutions, each with a different concentration from 10 to 100 μM. Additionally the valve could be easily switched to NaHCO₃ solutions or mixes of solutions, independent of the pH indicator. The use of a flow cell setup also allowed for more repeatable measurements compared to individual cuvette experiments. Tube lengths and flow rates chosen allowed for an analysis time of two minutes per sample. The setup used a 0.76 mm I.D. tube to transfer the pH indicator, a 1.03 mm I.D. tube for the NaOH solution and another 1.03 mm I.D. tube for the contaminant alkali solutions.

3. Results and discussion

Although the objective of this study is to determine the feasibility of pH indicators as microfluidic based online alkali mist sensors (following alkali trapping in an aqueous solution), the feasibility of simply using pH probes as sensors was also investigated. The data is presented and discussed below.

3.1. pH probes based measurements

To determine if direct pH-probe based measurements could be used as one of the methods for alkali detection, two different test scenarios were initiated. The first test involved logging the pH probe measurement within the first few seconds of the probe being immersed into the test solution, whereas the second scenario used a 1 min settling time before recording the value. For both experiments, measurements

Table 2
Indicators and solutions used for sodium hydroxide and sodium carbonate testing.

Dye	Dye Concentration (× 10 ⁻³ % w/v)	Solution	Concentration (μM)
Neutral Red	0.0041	Sodium hydroxide	10–100
Cresol Red	0.0045	Sodium carbonate	
Phenolphthalein	0.0225	Mix (NaOH + NaHCO ₃)	

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