

Monitoring of Anti-Caking Solution Preparation and Loading during Loadout Treatment of Potash Using FT-NIR

Mohammad Hussein and Adam Donaldson*

Process Engineering and Applied Science, Dalhousie University, Halifax, Nova Scotia, B3H4R2, Canada

Abstract

Fourier transform near-infrared spectroscopy is presented as a novel method for monitoring anti-caking reagent preparation and loading ratio on granular potash samples during loadout. Using commercial anti-caking agents and granular samples obtained from an operational loadout facility, amine weight percent in the anti-caking solution was determined between 0 and 7 wt% to an accuracy of \pm 0.1 wt%, while the loading ratio was determined between 0 and 4.3 lb/ton to within an accuracy of 0.1 to 0.3 lb/ton, depending on the sample heterogeneity. These errors are comparable to current analysis techniques, with minimal sample preparation and an analysis time of seconds. FT-NIR is thus presented as a novel monitoring method for these applications within the potash processing industry

Keywords: Amine content; FT-NIR; Anti-caking; Granular salt; Spectroscopy

Introduction

Potash is a potassium-rich fertilizer that facilitates plant growth, promotes pest and disease resistance, and improves the ability of plants to absorb and retain water and produce more crops [1,2]. Environmental conditions such as humidity and temperature impact the effectiveness of the stored fertilizers, where dust formation may occur over prolonged storage periods affecting the adsorption efficiency of plants [2]. Chemical additives such as long chain amine molecules, C₁₅-C₂₀, are introduced as anti-caking agents to prevent dust and cake formation during storage. The presence of liquid in fertilizers is one of the leading roles in cake formation, resulting vapour condensation due to temperature variations or liquid presence due to capillary forces [3-11]. Many studies have concluded that amine additives can be employed as a coating material to prevent dust and cake formation, such as the use of lauryl amine to reduce caking of ammonium perchlorate [12]. These additives function by inhibiting the growth of crystal bridges and the resulting caking that may occur [12-14].

In anticaking applications, the amine molecule is added to an light oil at weight percent ranging from 2 to 7%, after which the amine/oil mixture is spray-coated onto granular KCl within a loadout facility. The loading rate of the anti-caking agent applied may range by compound, but typically is near 1 to 2 kg of surfactant mixture per tonne of granular salt. This amount of added surfactant was enough to coat the entire surface area of the granular salt and prevent cake formation. Higher amounts of loading of the surfactant mixture could prove harmful since most amines used in this application have an LD₅₀ of 2.4 g/kg, and are considered toxic to marine life. Increased loading of the surfactant mixture also inhibits plant uptake of the potassium due to the increased hydrophobicity. To low a dosing will result in dust or cake formation during transport and storage, which may be considered off-spec and require the prepared product to be reprocessed.

From an operational perspective, it is important to be able to monitor both the surfactant preparation and loading rate prior to and during loadout. Given the amine-base, the surfactant content can be determined by titration, Baume Scale, or total organic contents, (TOC). Titration measurements can be subjective due to color interpretation by

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a lab analyst, and may introduce errors from volumetric determination of the amount of acid and base added. The use of strong acids or bases makes this measurement technique less attractive. The Baume scale is a density meter that can provide the density and temperature of the ammonia solution. By utilizing these two properties, the weight percent of ammonia may be correlated from several factors that may introduce errors within the final reading. For determination of the average loading on a given particle sample, the TOC method involves the addition of an acid to oxidize the organic carbon and produce carbon dioxide. The formed carbon dioxide is then measured by a detector. This technique requires that the reactions take place in the aqueous phase, suggesting that the technique can be replaced with a faster method. TOC technique requires a minimum of 10-15 minutes to complete a single measurement, with samples diluted by a factor of 2-50 depending on the type of reaction chosen. Further, a catalytic reactor would also be required for the oxidation reaction of the carbon.

This work demonstrates the novel application of Fourier transform near infrared (FT-NIR) as a measurement technique with sufficient accuracy to determine both the amine weight percent as well as the oil loading onto KCl. FT-NIR has been successfully used to monitor and characterize a variety of chemical processes [15-17], having a unique advantage in its ability to measure granular samples and the strong response of amine groups within the wavenumber range of this spectrum (10,000-4,000 cm⁻¹). Of specific interest is the three NH₂ overtone regions as well as the carbon-carbon overtones for the oil. Of these regions, the first and second overtones are examined in detail to provide accurate amine weight percent and oil loading onto the samples.

*Corresponding authors: Mohammad Hussein and Adam Donaldson, Process Engineering and Applied Science, Dalhousie University, 1360 Barrington St., Halifax, Nova Scotia, B3H4R2, Canada, Tel: 19024944035; E-mail: adam.donaldson@dal.ca

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Experimental Setup

Anticaking mixtures were prepared through the combination of a Tallow alkyl amine and a commercial light oil. The dispersing agent selected was a product of AkzoNobel, having an average molecular weight of 267 and a neutralization equivalent ranging from 258 to 269.

Anti-caking solution preparation

Amine-oil calibration standards were prepared at concentrations ranging from 0 to 7 wt% and mixture temperatures of 40, 50, and 60°C, sufficient to melt and maintain the mixture its liquid state. At each condition, a sample was collected in a 1 cm path length quartz cuvette and placed in a heated transmission cell within the Antaris II FT-NIR spectrometer. Full spectra were recorded to measure the absorbance as a function of both temperature and concentrations. 50 samples were taken in which 40 were used for calibration model development and 10 were used for validation. After model development, additional batches were prepared and examined against the calibration model to determine its accuracy. 15 scans were collected for each sample with a resolution of 4 cm⁻¹ in 6 seconds. The amine bond presented itself in the first (~5,000 cm⁻¹), second (~ 6,700 cm⁻¹) and third (~9,700 cm⁻¹) overtone regions.

Anti-caking loading on KCl

Granular product samples were provided by the Mosaic Company with variable surfactant loading ratios using the same surfactant/oil combination employed in this work. The loading rates tested were 0 (i.e., no treatment), 2.9 and 4.3 lb/ton. Additional heterogeneous samples were created through combinations of the received commercial samples (Table 1) to determine the impact of heterogeneity on the methods' ability to detect loading rates.

The samples were prepared in flat-bottom glass vials and placed on the integrated sphere module of the Antaris II FT-NIR system. 15 scans were collected for each sample with a resolution of 4 cm⁻¹ in 6 seconds. A background reference was also collected before the beginning of the experiment to ensure that any environmental changes within the lab were accounted for in the sample spectra. On average, 10 spectral sets were collected for each sample with the sample shaken between each set to vary the powder fraction being analyzed. This provided 70 spectra in total, of which 55 were used within the calibration model and the remaining 15 were used as validation points.

Results and Discussion

Armeen T in oil dosing

The complete spectra of the prepared surfactant-oil solutions are presented in Figure 1 with the second and third overtone regions indicated. The second overtone region was selected for analysis of the amine content due to absorbance varying significantly between 0.1 and 1 (i.e., 10 to 90%). Using a partial least square model for the analysis of the amine/light oil mixture, with a Savitzky-Golay filter for smoothing, spectral analysis was performed on the second overtone region with a wavenumber range of $6,700 - 6,390 \text{ cm}^{-1}$ (Figure 2).

Calibration models were subsequently developed using the TQ Analyst software for the first-derivative of the spectra with temperature corrections included, yielding an equivalency plot (Figure 3) and error residual plot for the range of temperatures and concentrations tested (Figure 4). Temperature was observed to impact the characteristic behaviour of the NH_2 bonds, decreasing light adsorption as temperature increased. A temperature-correction factor was applied within the TQ-Analyst software to counter the temperature's effect. The resulting

cross-validation factor of the calibrated model was 0.0445, with an independent validation, RMSEP, of 0.0333. The correlation coefficients of both factors were near 1, confirming NIR was an excellent analytical tool for monitoring amine content within the anti-caking agent solution. The resulting method was capable of determining amine weight percent to within 0.1 wt%.

Anti-caking agent on KCl

Through similar analysis of the full spectra for powder samples, the second overtone region of the CH and the CH_2 bonds (5,500-5,800 cm⁻¹) was selected in the analysis of loading of anti-caking agent on granular samples. It should be noted that in the presence of significant water content, it may be necessary to shift the focus of this analysis to the second overtone region used for the anti-caking agent, or that a ratio of this region and the 6,700-6,390 cm⁻¹ regions explored for amine content may enable single-point measurement of granular samples for both properties.

The CH/CH₂ region of interest exhibited two distinct peaks as loading ratios were increased (Figure 5), providing a viable reference from the raw spectra for calibration model development. Utilizing a partial least squares regression with four factors for the 5,500-5,800 cm⁻¹ regions, a calibration model was obtained for homogeneous and heterogeneous samples with the equivalency and residual error plots shown (Figures 6 and 7). The calibration model yielded a cross-validation factor, RMSEC, of 0.169 and an independent validation, RMSEP, of 0.085. The correlation coefficients of both factors, 0.992, and 0.996 suggested a good fit of the validation points to the calibration model with margins of errors of \pm 0.3 lb/ton of loading. Notice that the spread of the data was small for each homogenous sample mixture compared to the spread for the heterogenous mixtures, resulting in a larger overall error margin. If only the raw granular are used to develop the calibration model, the margin of error reduces to \pm 0.1 lb/ton.

Conclusion

Fourier transform near infrared spectroscopy was successfully applied to quantify Armene T content from 0 to 7 wt% in light oil at temperatures from 40 to 60°C, and to determine the loading ratio of anti-caking agent on granular potash samples from 0 to 4.3 lb/ton. The prediction error obtained for both weight percent and loading ratio were \pm 0.1 wt% and \pm 0.3 lb/ton, respectively. Where the error for amine content is comparable to traditional methods, and a loading ratio error of 0.3 lb/ton is sufficient to detect variations within the acceptable loading ratios range from 2.2 to 4.4 lb/ton, the use of FT-NIR is presented as a novel monitoring method for these applications within the potash processing industry.

| 0 lb/ton (g added) | 2.9 lb/ton (g added) | 4.3 lb/ton (g added) | Resulting Loading |
|--------------------|-------------------------|-------------------------|----------------------|
| 1 | 0 | 0 | 0 lb/ton |
| 0 | 1 | 0 | 2.9 lb/ton |
| 0 | 0 | 1 | 4.3 lb/ton |
| 1 | 1 | 0 | 1.45 lb/ton |
| 1 | 0 | 1 | 2.15 lb/ton |
| 0 | 1 | 1 | 3.6 lb/ton |
| 1 | 2 | 0 | 1.93 lb/ton |
| 1 | 0.5 | 0 | 0.97 lb/ton |

 Table 1: Composition of heterogeneous powder samples.

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Figure 5: Absorbance spectra of the CH and CH₂ functional groups observed for the raw granular samples.



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