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NIR-Based Simultaneous Measurement of Amine Loading and Degree of Neutralization during Flotation Reagent Preparation for Potash Processing

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Abstract

A continuous spectroscopy-based monitoring approach of the amine reagent preparation prior to flotation processing was investigated. The process involved the neutralization of a long carbon chain amine, C16-C20, with hydrochloric acid. Current methods of monitoring the degree of neutralization, controlling the HCl addition, and monitoring the amine content were based on pH measurements, with out-of-line sample lab-validation carried out using titration-based methods. Industry feedback indicated this method was prone to error and had resulted in challenges in process control. This work demonstrates a novel method of measuring both amine content and degree of neutralization using a mini-fluidic reactor and FT-NIR system equipped with a flow-through heated transmission cell. Analysis of the spectral response for wavenumbers in the range of 4,258-4,400 cm^{-1} yielded amine content and degree of neutralization measurements accurately to within ± 0.065 wt%, and ± 6.0% margin of errors, respectively. This led to monitoring intensification to increase KCl recoveries in flotation processing.

Keywords: Sorption materials; Wastewater; Chitosan; Zinc ions; Millet husk

Introduction

Aqueous amine solutions have been neutralized with HCl as part of the reagent conditioning process to separate KCl from NaCl in flotation vessels. The amine reagent, C-16 to C-20 hydrocarbon chain, is neutralized by the addition of HCl at an equimolar ratio to enable the protonated amine molecule to bind to the crystal defects in KCl, increasing its ability to attach to air as part of the flotation process. Batch conditioning of the amine reagent has demonstrated foaming tendencies and a lack of homogeneity of the final solution with respect to the degree of neutralization, (DON) of the solution. Due to mixing irregularities, complete protonation of the amine solution ($R\text{-}NH_2$ to $R\text{-}NH_3^+$) could not be achieved due to the formation of micelle globules that served as a protective layer against the protonation process [1]. The protective layer can be broken down by increasing the dispersion of the amine throughout the solution and maintaining constant agitation [2]. Batch to continuous conversion of this process is an on-going trend [3], but requires accurate monitoring of the neutralized amine solution to maintain suitable flotation reagent activity. Determination of the amine content and the amount neutralized has been done using titration-based measurements or the Baume Scale method. These two methods require added factors that affect the final measurements of the weight percent and the percent neutralized. There is also a need for dilution, drying, addition of additives, and pre-heating of the sample all in which will increase the margin of error (MOE) of the amine content and the DON. These techniques are also time consuming, labor intensive, and hazardous. Titration tests are inaccurate when the amine content must be within ± 0.001 g/g error margin. Baume scales are also as accurate as the introduced factors and cannot reach less than ± 0.01 g/g error margin.

Over 50% of potash production is achieved through flotation separation [4]. Many optimization studies have been done on the attachment of amine/KCl globule to air bubbles to enhance the separation [4]. It is crucial to note however that the amine must be homogenously neutralized for the attachment to take place. Amine molecules that are not neutralized will not bind to KCl crystals, and the amine recovery of KCl will significantly decrease across the flotation processes. Therefore, this paper focuses on the assurance of complete neutralization of the amine solution, along with a continuous monitoring method to regulate the flow of the reagent for recovery enhancement purposes. The near infrared spectral region has been used to monitor primary, secondary, and tertiary amines, with absorbance peaks for the first and second amine overtones occurring across the spectra for primary amines [5]. These absorbance peaks could be used to develop calibration models for the amine weight percent and it's DON. A primary amine loading onto silica as part of a molecular weight determination study has demonstrated the absorbance peaks and its variation with different loadings across the first overtone region ~4,950 cm^{-1} [6]. It has also illustrated the use of the partial least of square statistical method to develop a multivariate calibration model of the amine-containing loading in its liquid state onto silica [6]. This has demonstrated the applicability of using the Near Infrared region to measure the amine absorbance in the liquid form, and develop a calibration model to correlate between the absorbance and the amine content. The inline monitoring of amine has also been achieved through utilizing fiber optic cables to determine the reaction kinetics of amine in epoxy [7]. This is achieved through examining the characteristics of the absorbance peaks, and their respective appearance/disappearance as the reaction progressed [6]. The use of multivariate calibration models as monitoring methods has demonstrated durability and accuracy when compared to reference methods of monitoring [8-9]. High degrees of precision have been achieved in terms of monitoring pH, amine solutions, and hydrocarbon concentrations [6-11]. The use of in-line monitoring throughout continuous mixing of solution has been established in several studies [12]. Given that the FT-NIR can

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monitor the homogeneity of a solution, [13-16] it provides the means for testing out the homogeneity of solutions during mixing by in-line monitoring [12,16]. The Antaris II FT-NIR analyzer will be utilized to monitor both amine weight percent and DON in a mini-fluidic system specifically configured for continuous production partially and fully neutralized solutions. The measured absorbance will be used to develop a calibration model that will focus on the amine bond overtones as well as stretches in the carbon chain, C-C. The desired outcome is to intensify the monitoring process to calculate the degree of neutralization to increase the recovery of KCl in flotation separation.

Experimental Setup

Mini-fluidic reagent preparation

Flotation reagents of varying amine weight percent and DON were generated in a minifluidic system comprised of a water reservoir, dosing pumps for both amine and HCl, a shear-based mixer and 1/8" PFA tubing flowing into a transmission cell for spectral analysis (Figure 1). The chemicals involved were a C-16 to C-20 amine hydrocarbon and a hydrochloric acid solution with CAS# of 7647-01-0. For each experiment, tap water was heated to a set temperature between 50 and 70°C and stored in a reservoir sufficient to service each experiment. The amine weight percent and the DON parameters were varied through adjusting the dosing rate of the two syringe pumps. The amine weight percent was adjusted from 1.0 to 3.0 wt% with a dosing rate of 0.5 wt%, while the DON was varied for each chosen weight percent from 0% to 110% DON with a dosing rate of 10%. A DON of 100% represented a neutralization equivalence of ~260. The molecular weight of the reagent is obtained by multiplying the neutralization equivalence by the number of basic functional groups that require neutralization within the reagent. Since there is only one basic functional group in the reagent, $R\text{-}NH_2$, and that the molecular weight is equal to the neutralization equivalence, then a DON of 100% represented a molar ratio of 1:1 between amine and HCl. The flotation reagent was initially heated to a matching temperature and drawn into an electrically-traced steel syringe. The molten reagent was then injected into the water stream prior to entering a shear-based mixer (Micropump P23 head installed on a magnetically coupled drive operating at 300 mL/min). A diluted 4.5 M HCl solution was injected at variable rates depending on the desired DON. Hot water was initially run through the PFA tubing to pre-heat the system and prevent any solidification of amine throughout the lines. Following pre-heat, HCl was injected at an equimolar flow rate to that of the amine, where it was adjusted then to reach the desired degree of neutralization. The solution then passed through a gear pump and 3 m length of 1/16" ID PFA tubing with a residence time of ~25 seconds for neutralization to occur. Note that initially a fiber optic probe was utilized at multiple points along the PFA tube to determine if the neutralization reaction could be tracked, but it was quickly determined that the spectra did not vary along the 3.0 m length, suggesting that neutralization between the amine reagent and the HCl solution was instantaneous. The reagent solution was thus directed through a flow-through heated transmission cell with a path length of 1 mm for subsequent analysis in the Antaris II FT-NIR unit.

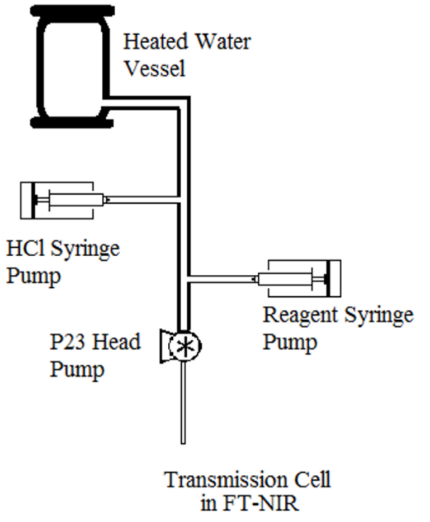

Figure 1: Schematic of the mini-fluidic setup of the reagent preparation and its monitoring.

Spectral analysis

Since the solution was comprised of an amine molecule, the focus then was on the three overtones of the $R\text{-}NH_2$ bond. The examined wavenumber range was 10,000-4,000 cm^{-1}. Water was included in the background reference to negate its effect on the amine absorbance. The focus of the spectra was on the first overtone region (~4,900 cm^{-1}), the second overtone region (~6,600 cm^{-1}), and the third overtone region (~10,000 cm^{-1}). Furthermore, the absorbance region in the range of 4,000 cm^{-1}-4,500 cm^{-1} was thoroughly examined because of the presence of a distinguishable trend in the spectra. For each experimental set, samples were collected and analyzed using the accepted quality-assurance methods of the industry partner to determine the amine weight percent as well as the neutralization percentage using both diluted HCl and KOH solutions. These measurements were used and referred to in this paper as the actual amine weight percent and the actual degree of neutralization. The water flow rate was held constant throughout the experiment, but the amine and the HCl flow rates were adjusted to provide a wide range of data. The use of the C-C bond chain wave number region was also explored to examine its capability in developing a model. A background spectra of heated water was initially taken to ensure that any environmental changes within the lab were accounted for in the sample spectra. 50 samples were taken in for each weight percent, with 5-10 validations points utilized for each. 10 scans were collected then averaged for each measurement with a resolution of 4 cm^{-1}. A partial least square analysis (PLS) was utilized for the basis of absorbance calibration on the wavenumber region chosen for the analysis, 4,400-4,250 cm^{-1}.

Results and Discussion

The amine overtones were examined to determine the amine weight percent in the neutralized solution (Figures 2-4) represent the three overtones of the amine bond for 1, 2, and 3 wt% at varying DON. The data was analyzed using the Antaris II software to provide a calibration model that predicts the weight percent and DON, but none of the models provided the minimum required accuracies with respect to the two parameters. These three overtones were utilized separately and together to obtain a best-fit model. A smoothing Savitzky-Golay polynomial filter was used to decrease the amount of noise. In the first overtone spectra, a shift in the absorbance minimum peak was observed from wavenumbers 5,250 cm^{-1} to 5,350 cm^{-1}. This shift took place as more of the amine was neutralized that also resulted in a decrease in the absorbance magnitude as seen in the 1st overtone across Figures 2-4. Across the 2nd overtone for the three figures, an increase in the absorbance magnitude around ~6,750 cm^{-1} was observed with higher degrees of neutralization, but the opposite trend was observed across an amine content of 1 wt%.

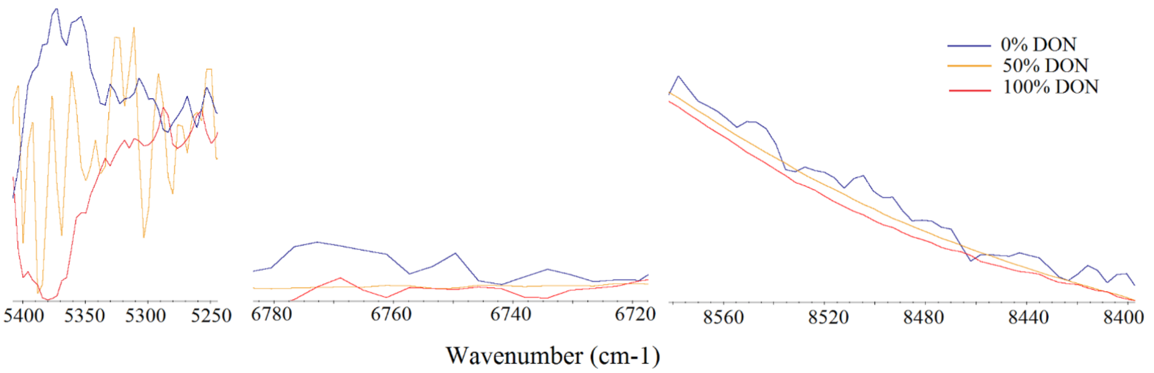

Figure 2: The three overtones for 1 wt% of amine at three different DON%. 1st overtone (left), 2nd overtone (middle), and 3rd overtone (right).

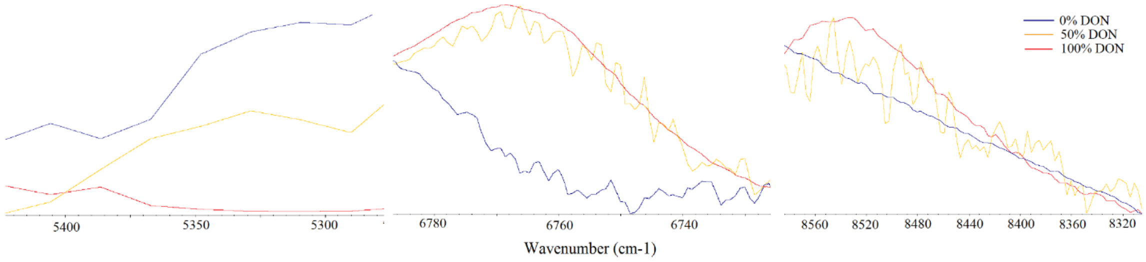

Figure 3: The three overtones for 2 wt% of amine at three different DON%. 1st overtone (left), 2nd overtone (middle), and 3rd overtone (right).

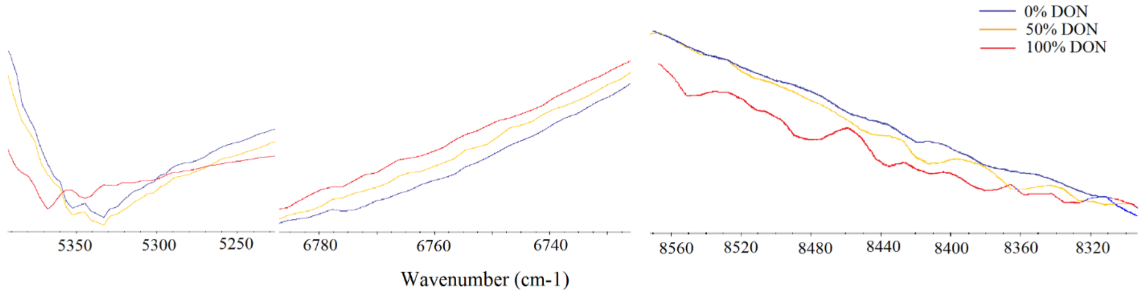

Figure 4: The three overtones for 3 wt% of amine at three different DON%. 1st overtone (left), 2nd overtone (middle), and 3rd overtone (right).

Lastly, the most noticeable change of absorbance was observed at the 3rd overtone region. In Figure 4, 0% DON had the highest peaks at 8,650 cm^{-1}, whereas higher degrees of neutralizations had lower magnitudes.

A calibration model using these three overtone regions was developed to assess how useful these overtones could be in determining the degree of neutralization of the solution. Figures 5 and 6 represent the calibration model developed along with its residual error plot. The calibration model was unable to predict the degree of neutralization within the required minimum margin of error of ± 5% DON obtained through titration-based measurements. Although there were trends observed as the degree of neutralization changed, these trends were not consistent throughout the absorbance spectra. Given that a constant flow rate of water was taken within the background reference, minimal changes to that flow rate would have a visible effect on the absorbance. Due to these minimal changes, the absorbance of amine and water overlapped across the 1st, 2nd and 3rd overtones. This overlap resulted in the observed noise in Figures 2-4. A different wavenumber region was explored to calculate the amine weight percent and it's DON. It was noted that the region of 4,400-4,250 cm^{-1} was not affected water overtones, improving signal to noise ratios within that region. Increases in the DON increased the absorbance of the C-C bond present in that region. Over additions of hydrochloric acid did not impact the spectra which made it more appealing to use as the basis to develop the multivariate calibration model rather than the use of the three amine overtones.

In theory, neutralization of the amine to an ammonium ion increases the attraction forces between the ammonium ion and the carbon electrons due to increases in electronegativity differences [17-18]. This pulling of the electrons towards to the ammonium ion shrinks the carbon chain and is thought to decreases its absorbance, as seen at wavenumbers 4,292 cm^{-1} and 4,400 cm^{-1}. The decrease of the absorbance in this region however, and not across other regions, is not clearly understood yet.

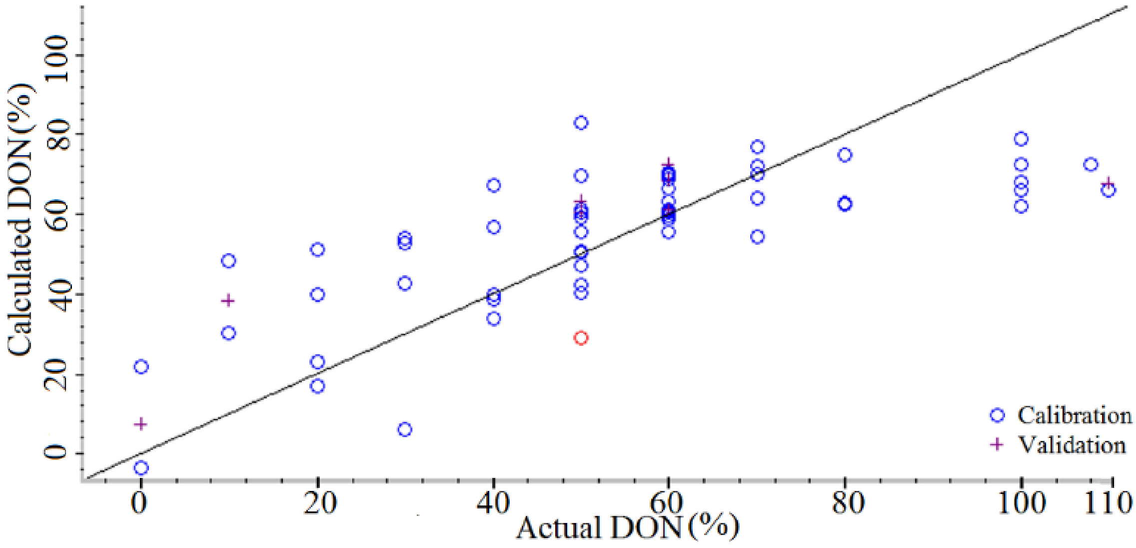

Figure 5: A calibration model using the three amine overtone regions after smoothing filters were applied.

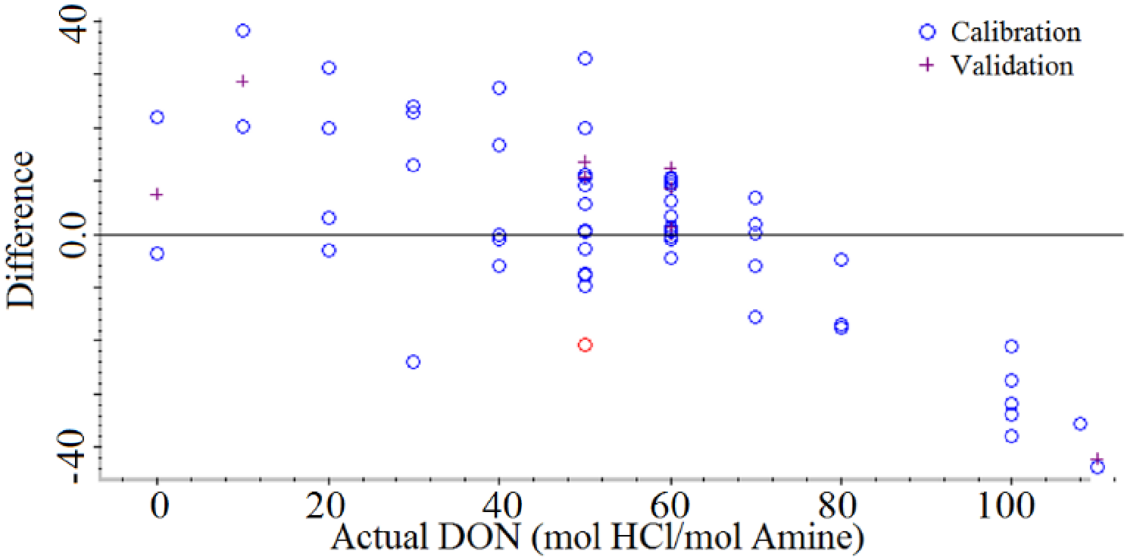

Figure 6: Residual error plot using the three overtone regions of amine after smoothing filters were applied.

The model for the three amine weight percent managed to predict the DON with a root mean square error of calibration of 7.17% and a root mean square error of prediction of 6.33. This was achieved by utilizing the Savitzky-Golay polynomial filter to reduce the noise in the spectra. The correlation coefficients for each were 96.6% and 99.0% respectively. The TQ Analyst software model predicted the DON with a MOE of ± 6%. Figures 7 and 8 represented the calibrated Antaris model for the DON and its residual error difference. The weight percent calibrated model through the software provided resulted that were within the required accuracy. As seen in Figures 9 and 10 a margin of error of $\pm 6.5 \times 10^{-4}$ g/g was achieved.

The amine weight percent and the DON multivariate calibration models provided in-line monitoring methods of the neutralization reaction with precision results that are better than that of the reference methods, but with no sample manipulation and minimal labor work. The modification of the monitoring method from a titration-based one to an in-line continuous spectroscopic-based one intensifies the reagent preparation process, and in return increases the recovery of KCl in the flotation process.

Conclusion

The Antaris II FT-NIR analyzer was utilized to develop multiple models to predict both the degree of neutralization and the amine weight percent as part of the reagent conditioning in flotation processing. The absorbance was measured using a built-in heated transmission module equipped with a flow-through cell to measure the absorbance of the solution. The results demonstrated a calibration model that relied on

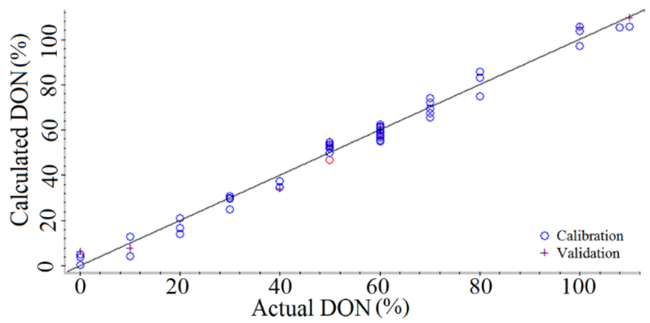

Figure 7: Calculated *vs*. actual DON for amine weight percent 1, 2, and 3 wt% using Antaris software.

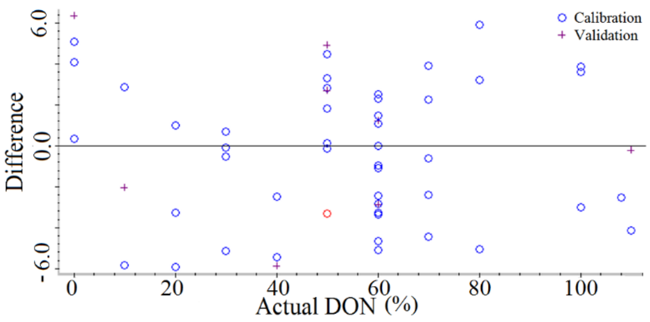

Figure 8: Residual error difference of the DON data for mass fractions 1, 2, and 3 wt%.

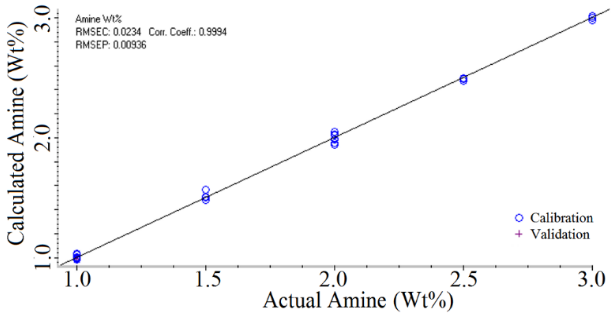

Figure 9: Calculated *vs*. actual weight percent using the Antaris software.

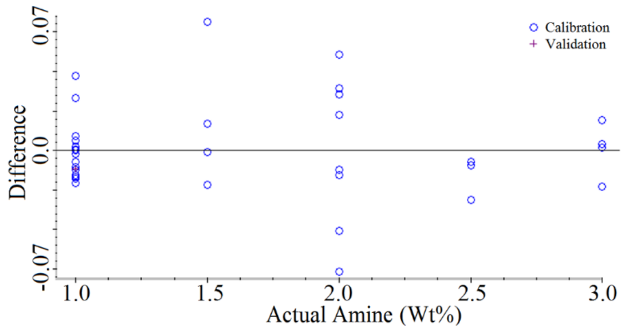

Figure 10: Residual error plot for the amine weight percent calibrated model using the Antaris software.

the absorbance in the region of 4400-4258 cm^{-1} to calculate the amine weight percent and its degree of neutralization to within 0.065 wt% and 6% DON, respectively. The continuous in-line monitoring could lead to process intensification where deviations of the DON away from the set point could be instantly corrected without out-of-line sampling taking place. Currently, deviations of DON away from the set point translate into low recoveries of KCl within the flotation process, where the average recovery is ~70%. The potential to increase these recoveries lies within increasing the DON of the amine solution to 100%. Continuous monitoring of the amine reagent preparation, and across the flotation process, would increase the recovery of KCl beyond an average of 70%.

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