

Fertilizer Mixer Performance Evaluation Using Chloride Titration

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Abstract

Mixing processes are a critical step in manufacturing blended fertilizer products. Although each stage of the production process is monitored to prevent deficiencies and ensure quality in fertilizer production, evaluation of mixing performance by regulatory agencies are the keys to assessing quality of the final product. The Office of the Texas State Chemist (OTSC) conducted a fertilizer mixer evaluation study, which involved two main components: sample collection and lab analyses. Samples from 9 mixers were collected from 7 fertilizer manufacturing locations in Texas. Firms were selected based on the type of fertilizer components currently in use and the type of mixer(s), which included cement type, vertical, volumetric and paddle. Sample collection follows the process outlined by The Fertilizer Institute (TFI). Samples are collected from the blended product and from the individual raw ingredient materials. In the laboratory, the samples from the individual raw materials and blended product stream cut samples were analyzed for size guide number (SGN), density, particle number, and nitrogen (N)-phosphorous (P)-potassium (K) levels, and Chloride (Cl-) content. The sample accuracy was calculated by comparing the actual formula weights to the expected values for the blended product. To determine mixer efficiency and reproducibility, coefficient of variations were calculated to determine the variability between various samples of the blended product. Our results indicated Cl- titration is a cost effective method to efficiently evaluate mixer performance, the mixing time of tested cement mixer may result in high variation in the N-P-K analysis, and Cl- level in blended samples. Based on our previous feed mixer study, facilities operating these cement mixers may consider to check mixer readiness and increase mixing time to achieve better homogeneity.

Keywords: fertilizer mixer, performance evaluation, blend, homogeneity, N-P-K, chloride

1. Introduction

Fertilizer is either the natural or synthetic originated material applied to growing media to promote plant growth. Fertilizers typically provide various proportions of nutrients, including main macronutrients, and other micronutrients [19].

Three main macronutrients in fertilizers are nitrogen (N), which enhances leaf growth; phosphorus (P), which induces root development; and potassium (K), which promotes stem growth, flowering, and fruiting [1, 5, 17]. The three secondary macronutrients consist of calcium (Ca), magnesium (Mg), and sulfur (S). Micronutrients include copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), boron (B), silicon (Si), cobalt (Co), vanadium (V), and other mineral catalysts [22].

The homogeneity of the fertilizer is critical to ensuring the consistent delivery of nutrients to the plants. Segregation and mixing phenomenon generally occur in most powdered or granular solids systems and have a significant influence during the mixing process [18]. Understanding particle flow and mixing in a blender is important for optimal design and operation.

Since product performance depends on blending homogeneity, variability in mixing operations can be detrimental to manufacture quality. Efforts along these lines include the development of Discrete Element Method (DEM) based on numerical models used to simulate granular flow within mixers. Digitally-recorded mixing states from experiments are used to fine-tune the numerical model. Parametric study of the effect of initial loading, particle size, fill ratio, and vessel speeds are investigated with tracer experiment and numerical simulation. Intriguingly, the particle size and fill level are found to have no significant effect on mixing characteristics in some studies [4, 18]. However, these models may not be readily applicable for feed and fertilizer mixer studies.

Since 1929, some mixer research has been done [7]. However, mixing remains a critical but under-characterized aspect of manufacturing fertilizers. The first step to evaluating mixer performance is to determine the optimum mixing time and collect representative samples. Mixing is expected to vary with batch sizes, particle shapes, and ingredients. It is also necessary to know the time it takes to discharge the mixer and calculate reasonable sample collecting time [9]. In a previous report on feed mixers, defects in mixer design, overfilling, insufficient mixing time, and electrostatic effects were found to result in incomplete

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mixing in both vertical and horizontal feed mixers. Overfilling a feed mixer can influence the mixing action of ingredients at the top of the mixer in horizontal mixers. In addition, mixing below 50 percent of its rated capacity can also reduce mixing action [12]. Solutions to improve and evaluate mixing performance were also suggested in this feed mixer report.

Other studies on feed mixers [10, 12] indicate that identifying a standard procedure to collect representative samples from different types and designs of horizontal and vertical mixers presents a challenge [13]. For example, samples can be taken from the spout end of portable grinders/mixers or near the discharge point for a vertical mixer. Horizontal mixers are usually accessible from the top, which permits sample collection directly from the mixer using a probe. Samples should be drawn at even intervals during mixer discharge and as close to the mixer discharge as practically possible, given safety constraints. The sampling time is calculated as total mixing time divided by 10 apart with the first stream cut sample taken a few seconds after the discharge begins [12, 23]. The stream should be cut quickly and evenly every time, with each cut being put into a separate container and sent to a competent laboratory for analysis.

Evaluating fertilizer mixer performance is even more complicated than for feed mixers. While producing multi-nutrient fertilizers, such as compound fertilizers, chemical reactions may occur among components. These chemical reactions are an additional source of variation in nutrient component levels [6, 8, 11, 16]. Due to this complexity and changes to component particle characteristics (such as by breakdown) in the blended fertilizer product, analysis of N-P-K has been suggested as a basis of evaluation. In an N-P-K analysis, actual formula weights are used to calculate the expected value for the blended product. After the results are obtained, a simple statistical analysis is performed [9]. Since the raw materials have been analyzed, along with the stream cut samples, the weights, average analyses of each material, as well the standard deviation (SD) and relative standard deviation (RSD, or % RSD) are calculated. SD is a measure of data variability around mean of a sample of population. The most common descriptive statistics is mean and SD, and for data not following the normal distribution in the form of “mean \pm SD”. RSD is the absolute value of the coefficient of variation (CV). The equation to calculate RSD is as follows:

$$\text{RSD} = \text{SD} / \text{m} \times 100$$

$$\text{m} = \Sigma X / n$$

X = Test value, m = mean / average of the test values,

ΣX = sum of the test value, n = number of sample,

SD = standard deviation

The RSD is useful and often necessary when comparing variability between measures with different absolute magnitude. The equipment problems, such as worn mixing spiral/paddle, mixer vibration, scale malfunction, misreading, or problems in obtaining and analyzing the samples, may result in high variance with the calculated analysis of the stream sam-

ples [9, 12]. In an ideal situation, there would be no or low significant difference between the stream samples. In order to determine how much variability is acceptable, a simple t-test and correlation test for the desired analysis of mixer homogeneity should be performed. Despite the complexity of fertilizer samples and potential chemical reactions that may occur during the blending process, we focused on percent variation of tests, including size-guide number (SGN), density, particle count, N-P-K analysis, and Cl- content, to determine the fertilizer mixer performance in this study.

2. Materials and Methods

2.1. Sample Collection

The selection of fertilizer mixer and sampling was influenced by the availability of blends manufactured at the time of the study, as well as the following factors:

1. Mixer type - Selected mixers represent the variety of equipment utilized by the Texas fertilizer manufacturers. None of the mixers had a surge bin before or after the mixer. The volumetric mixer was programed for a set blending time adjusted to the weight of the batch. All of the other mixers utilized a continuous process to blend as the mixers were loaded and unloaded.
2. Batch size - Samples were only collected from fertilizer batches that utilized $\geq 50\%$ of the overall capacity of the mixer.
3. Components - Fertilizer samples included some combinations of urea, ammonium nitrate, ammonium sulfate, diammonium phosphate (DAP), monoammonium phosphate (MAP), muriate of potash (K). One sample did not contain phosphate (P). One sample included Mosaic[®] MicroEssentials[®] SZTM (MESZ), which contains nitrogen, phosphorus, sulfur, zinc and filler. Samples with other types of added microelements were not collected as part of this study.

At the request of industry representatives serving on the Office of the Texas State Chemist (OTSC) advisory committee, the Texas Feed and Fertilizer Control Service (FFCS) and Agricultural Analytical Service (AAS) coordinated with fertilizer manufacturers in Texas to evaluate mixer performance. In the spring of 2016, FFCS field staff collected samples from nine mixers at seven fertilizer manufacturing locations in Texas (Table 1).

Sampling was performed as described in the TFI Bulk Blend Quality Control Manual blending performance procedure [9]. Both the cleanliness of the mixing system and the functionality of the scale and all required equipment need to be confirmed. Samples of each material being weighed and charged to the mixer, and at least 10 stream-cut subsamples from a location close to the mixer discharge at equally spaced time intervals need to be collected. Each subsample (average 600 g) was placed into a separate sample collection bag and marked to denote the sequence of collection. Each component sample (average 4.5 kg) was placed in a separate bag and labeled with

Mixer	Facility	Mixer Type	Capacity (tons)	Mixer Age (yrs)	Product (N-P-K)
1	I	Cement	8	25-30	23-11-11
2	I	Cement	5	20-25	35-5-10
3	II	Cement	8	6	28-7-2 with 1.94% S & 0.19% Zn
4	III	Vertical	4	1	24-6-12
5	IV	Vertical	6	unknown	20-10-10
6	V	Vertical	5	11	24-8-16
7	VI	Vertical	8	~12	25-8-8
8	V	Volumetric	unlimited	1	24-8-16
9	VII	Paddle	5	~8	26-0-26

Table 1: Information of collected fertilizer products and mixer types.

the name of the material. FFCS field staff submitted component and stream-cut samples to the AAS for sample preparation and analyses.

2.2. Size Guide Number (SGN) Analysis

Particle size is the most important factor in the selection of non-segregating materials. The SGN Scale is generally used in the field to select size-compatible materials, prevent segregating blends, identify the increased risk of poor mixing, and process control [9]. The SGN Scale (Sylvite, Lewistown, PA) is a device designed for simple particle size screen tests of fertilizer samples. The SGN determination process starts by transferring a representative sample of approximately 200 ml to the right end compartment of the SGN Scale, closing the SGN Scale, and rotating the scale to shake the sample in the top position until it has finished sifting. Samples with different particle size are separated by five fitted sieves. When the scale returns to the horizontal position, it directly produces a size histogram of the tested sample. SGN can be calculated by adding each median particle size per compartment times 100.

2.3. Density

Density is defined as the mass per unit volume of a material. Three types of density measurement can be determined for fertilizer products and fertilizer raw material: bulk density, apparent density, and true density. Bulk density is the most commonly used density value for fertilizer. Bulk density is determined by weighing a container of known volume filled with sample to the full level. In this study, the bulk density (oz/pt) was calculated as the weight divided by the sample in a one-pint measuring cup [14].

3. N-P-K Analysis

All fertilizer samples were ground using a Retsch ZM200 grinder with 0.75-mm screen, followed by four corner mixing process, and filled into one 4-oz sample bottle.

3.1. Nitrogen Combustion Analysis

A 0.05- to 0.1-g sample of dry fertilizer is weighed, combined with three times the sample weight of powdered sucrose, encapsulated in aluminum foil, and placed in the crucible of a FP-528 nitrogen determinator (LECO Corporation, St. Joseph, MI) set at 950 ± 25 °C. The sample is burned completely in a purified oxygen stream, and the gas flow is then passed through different reagents and filters to remove halogens, salts, and ash. A 10-ml aliquot of the gas flow is taken and passed through columns containing copper, nitrogen catalysts, CO₂ absorbent, and desiccant. These remove all remaining O₂, convert all nitrates/nitrites to N₂, and remove all CO₂ and H₂O, leaving only nitrogen and the carrier gas to pass through the thermo-conductivity cell detector. The difference in conductivity between the sample and reference lines is reported as % nitrogen [2, 20]. The combustion unit reports a % nitrogen measurement by an internal calculation using the following equation:

$$\frac{(Area \times Calfactor \times Kfactor)}{(SMPWT)} - (Blank/2) - AtmBlank \quad (1)$$

Equation (1): Area represents area of sample, Cal factor represents calibration factor, K factor is ballast pressure at start of analysis divided by 975, blank is the system blank at every calibration, Atm Blank is the atmospheric blank that set during instrument installation, SMPWT is sample weight in grams.

3.2. P₂O₅ Gravimetric Analysis

Available phosphorus (P₂O₅) is serially extracted from 1.0 g of fertilizer matrix with water and neutral ammonium. Once extracted, an aliquot containing up to 24 mg P₂O₅ is hydrolyzed to produce orthophosphate and react with quinoline molybdate to precipitate quinolone phosphomolybdate. Quinolone phosphomolybdate is then dried and weighed. The sample weight and the precipitate weight are used to determine the P₂O₅ level [2].

Percent available phosphorous in fertilizer is calculated using the following equation:

$$\%P_2O_5 = \frac{(CRWT2 - CRWT1) \times (1603.50)}{(SMPWT) \times (ALIQ1)} \quad (2)$$

Mixer	Ammonium		DAP	MAP	MESZ	Potash	Filler
	Urea	Nitrate					
#1		233	263			306	
#2	302		322			262	247
#3		315			285	227	281
#4	283		224	281		279	
#5	280		227	328		241	
#6	295		227		257	302	
#7	295		242	275		262	
#8	295		223		275	285	
#9	270					276	

Table 2: SGN determination of ingredient materials for each tested mixer.

Equation (2): CRWT2 is the weight of the Gooch plus precipitate in grams, CRWT1 is the weight of the empty Buchner Funnel with Fritted Disc in grams, ALIQ1 is aliquot taken from the extraction in mL, SMPWT is the weight of the sample in grams. 1603.50 comes from the conversion factor (0.03207) to convert $(C_9H_7N)_3H_3 [PO_4]_{12}MoO_3$ to P_2O_5 times 500-volume of extract in mL times 100-percentage factor.

3.3. K_2O Absorption Spectrophotometric Analysis

Samples (2.5 g) are weighed into a 250-mL volumetric flask containing 50 mL ammonium oxalate, 125 mL water, Antifoam B Silicone Emulsion (Sigma-Aldrich Inc., St. Louis, MO), and boiling chips. Samples are boiled for 30 minutes and filled to 250 mL with deionized water, and inverted at least 10 times to mix. Once the solids settle, the sample is filtered through Whatman filter paper. The filtered sample is transferred into a 100-mL volumetric flask, using 5 mL of 3% cesium chloride ($CsCl$) solution, filled to volume with deionized water, and the flask is inverted at least 10 times to mix. Additional filtration would be necessary if the sample becomes cloudy [2]. Samples and reference standards are analyzed using a Varian Spect 220FS or equivalent atomic absorption (AA) spectrophotometer. The atomic absorption readout is in parts per million (ppm) K, and must be converted to K_2O level. The % K_2O is calculated as follows:

$$\%K_2O = [(2.5)(PPM)/(ALIQ1)(SMPWT)] \times 1.2046 \quad (3)$$

Equation (3): PPM is the ppm reading from AA, ALIQ1 is the aliquot of each sample (mL), SMPWT is the sample weight (g), 1.2046 is the conversion factor from K to K_2O .

3.4. Chloride Titration

Water-soluble chloride is potentiometrically determined by 848 Titrino plus complete titrator (Metrohm Inc., Tampa, FL) with silver nitrate using a silver-indicating electrode. A 5.8-gram sample is dissolved in boiling deionized water, acidified with nitric acid and titrated with standardized silver nitrate [3, 15, 21]. Results are reported as percent chloride. The % Cl- is calculated as follows:

$$\%Cl^- = \frac{[mLTIT \times (AgNO_3) \times 35.453 \times 250 \times 100]}{(SMPWT \times ALIQ1 \times 1000)} \quad (4)$$

Equation (4): mLTIT is the volume of $AgNO_3$ in mL used in titration, $(AgNO_3)$ is the normality of $AgNO_3$ used, SMPWT is the sample weight in grams, ALIQ1 is the aliquot taken in mL.

4. Results and Discussion

In a previously conducted feed mixer study by the authors, less than 10% RSD in the assay procedure was considered to be excellent mixing. A RSD between 10% and 15% was considered a good mixing performance. A mixer rates was a fair performer if the RSD was between 15% and 20%. More than 20% RSD was considered as poor mixing performance. We applied the same criteria for fertilizer mixers in this study.

4.1. Physical Examination - Particle Count, SGN and Density

Urea particles counts ranged from SGN 270 to 302 (288.6 ± 11.2), with 3.88% RSD (Table 2). The SGN of ammonium nitrate ranged from 233 to 315 (274.0 ± 58.0), with 21.16% RSD, ammonium sulfate ranged from 223 to 242 (228.6 ± 7.7) with 3.37% RSD. DAP ranged from 263 to 328 (293.8 ± 29.3) with 9.97% RSD, MAP from 257 to 275 (266.0 ± 12.7) with 4.78% RSD, MESZ SGN-285. SGNs of fillers used in two cement mixers were 247 and 281 (271.1 ± 26.1) with 9.11% RSD. Potash ranged from 227 to 306 in all nine mixers (264.0 ± 24.0) with 9.64% RSD. Mixer # 1~3 represent evaluated cement mixers; mixer # 4~7, vertical mixers; mixer # 8, volumetric mixer; and mixer # 9, paddle mixer.

Density (oz/pt) of urea raw materials ranges from 0.48 to 0.51 (0.49 ± 0.01) with 2.57% RSD. Ammonium nitrate ranges from 0.63 to 0.65 (0.64 ± 0.01) with 2.21% RSD, ammonium sulfate from 0.60 to 0.72 (0.65 ± 0.05) with 7.14% RSD. DAP ranges from 0.57 to 0.64 (0.60 ± 0.03) with 4.49% RSD, MAP from 0.66 to 0.67 (0.67 ± 0.01) with 1.06% RSD, MESZ for 0.66. Density of fillers ranges from 0.79 to 0.84 (0.82 ± 0.04) with 4.34% RSD. Potash ranges from 0.68 to 0.76 in 9 mixers (0.72 ± 0.03) with 3.83% RSD.

Mixer	Ammonium		DAP	MAP	MESZ	Potash	Filler
	Urea	Nitrate Sulfate					
#1		0.63	0.57			0.70	
#2	0.48		0.60			0.68	0.84
#3		0.65			0.66	0.74	0.79
#4	0.51		0.60	0.64		0.69	
#5	0.48		0.68	0.60		0.71	
#6	0.51		0.64		0.67	0.73	
#7	0.50		0.72	0.58		0.73	
#8	0.49		0.63		0.66	0.75	
#9	0.49					0.76	

Table 3: Density (oz/pt) measurement of ingredient materials for each tested mixer.

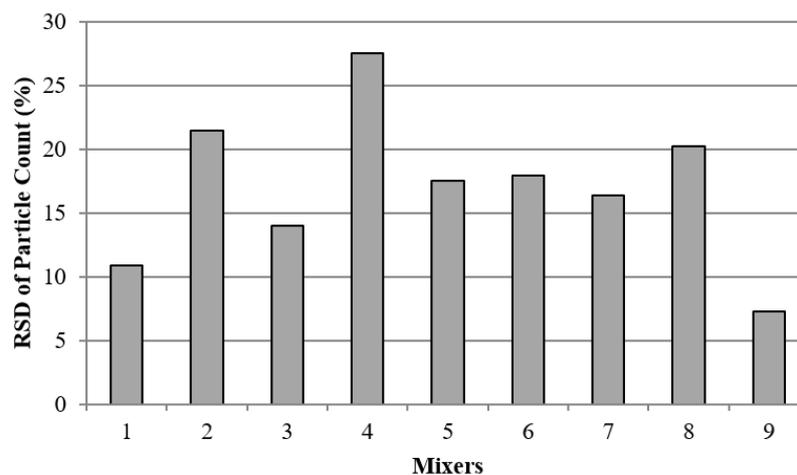


Figure 1: Variation of particle number in stream samples of nine fertilizer mixers.

Since tested fertilizer samples consist of different materials, evaluating fertilizer mixer performance through SGN and density are not well suited as metrics for comparison (Table 3). In addition, changes in shape and size of particles during the blending result in difficulties to use particle number to evaluate sample homogeneity. Particle number per gram were counted and results showed the particle numbers range from 65 particles to 128 particles per gram, standard deviation (SD) from 4.7 to 34.6, and % RSD from 7.3% to 27.5%. Based on the above results, variation in particle characteristics during production may also be poorly suited for evaluating fertilizer mixer performance (Figure 1).

4.2. N-P-K Analysis

For N analysis of the tested 10 subsamples, all evaluated mixers showed less than 10% RSD and indicated excellent performance in nitrogen-source ingredient mixing. In particular, seven out of nine mixers showed less than 5% RSDs. The RSDs for the evaluated mixers were as follows: 3.0%, 2.4%, 5.6%, 1.3%, 1.4%, 7.7%, 4.8%, 3.8%, and 3.5%. In P-analysis, the RSDs for the evaluated mixers are 9.3%, 17.2%, 20.8%, 4.5%, 9.3%, 13.4%, 3.7%, and 5.6%, respectively. Three out of four (75%) vertical mixers showed excellent mixing, with less than

10% RSD, and one mixer (25%) showed good performance, with 13.4% RSD. One out of three cement mixers (33%) had excellent mixing; another one (33%) had fair performance, with 17.2% RSD, and the other (33%) had poor performance, with 20.8% RSD. Samples collected from volumetric mixers showed excellent performance, with 5.6% RSD. For K analysis, one out of three cement mixers (33%) had excellent performance, with 4.2% RSD, and the other two mixers (67%) had poor performance, with 20.9% and 29.1% RSDs. In vertical mixer, three out of four mixers (75%) had excellent mixing, and one (25%) had fair performance, with 16.0% RSD. Both volumetric and paddle mixers had excellent performance, with 2.9% and 3.8% RSDs, respectively. The RSDs for the evaluated mixers were the following: 4.2%, 20.9%, 29.1%, 1.6%, 4.6%, 16.0%, 4.5%, 2.9%, and 3.8% (Figure 2).

4.3. Chloride Level Determination

Salt has previously been established as a recommended micro-ingredient to determine feed mixer performance based on its high density (75 lb/ft³) compared to corn (45 lb/ft³) [12]. Potash is a general term used to describe a variety of potassium-containing materials used in agriculture, the most common being potassium chloride (KCl). The chloride level was measured

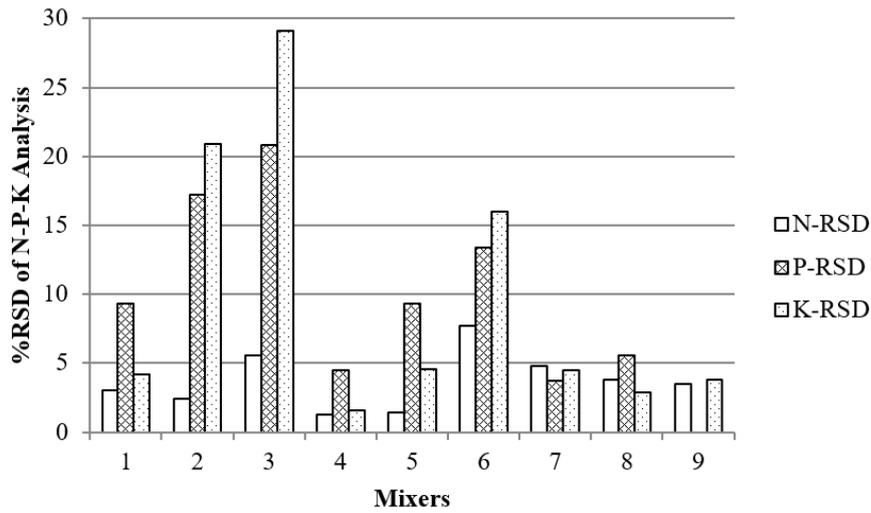


Figure 2: Variation of subsamples from the N-P-K analyses.

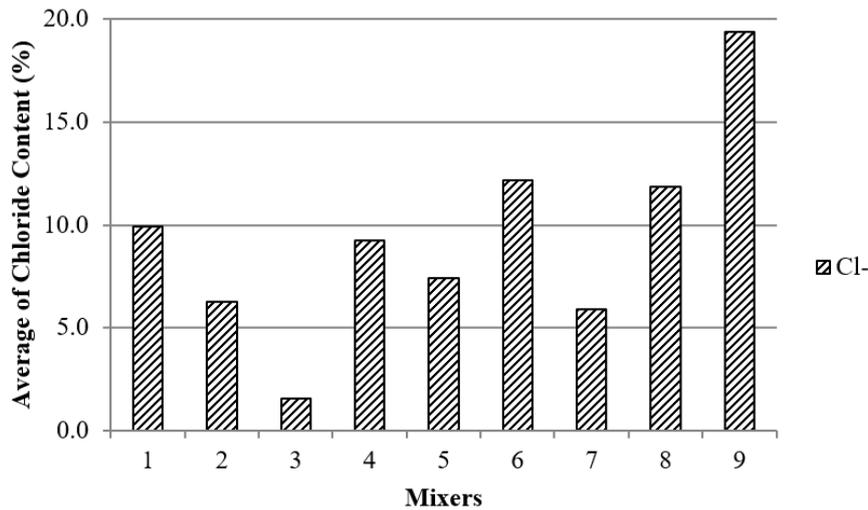


Figure 3: Chloride level for sample collected from the evaluated mixers.

by titrating with silver nitrate. Ten subsamples collected by each mixer were measured in duplicated sets and the average was calculated. In cement mixers, the averages were 9.9%, 6.3%, and 1.6%. In vertical mixers, the average chloride levels were 9.3%, 7.4%, 12.2%, and 5.9%; 11.8% chloride for volumetric mixers; and 19.4% for paddle mixer samples (Figure 3). The RSDs for each evaluated mixer were 5.4%, 20.6%, 27.8%, 2.0%, 4.8%, 16.1%, 6.7%, 3.5%, and 4.8%, respectively. Average of RSDs for 10 subsamples per mixer was also calculated.

Based on this evaluation, both volumetric and paddle mixers showed excellent performance with 3.5% and 4.8% RSD. Two out of 3 cement mixers had poor performance, with 20.6% and 27.8% RSD, and one performed excellently with 5.4% RSD. Three out of four vertical mixers had excellent performance and only one had fair performance, with 16.1% RSD (Figure 4).

5. Discussion

In the fertilizer industry, various types of mixers have been used to blend fertilizer. Analyzing mixer performance is complicated by different fertilizer products and types of mixers. In this study, samples were collected from four different types of mixers. In our analysis, we found that the general particle characterization methodologies, including SGN, density, and particle count, do not significantly correlate to the N-P-K analysis.

The average of N-P-K analysis results was also compared to fertilizer labels (Figure 5). This accuracy test indicates two cement mixers have lower accuracy (>10% variation) in potassium contents. Two cement mixers and one vertical mixer also showed lower accuracy in phosphorous levels. For the most part, the accuracy test confirmed our performance study; although, we confirm that fertilizer mixer performance could be evaluated by the K levels with variation. One particular cement mixer (#1) shows lower variation but has low K accuracy. Fur-

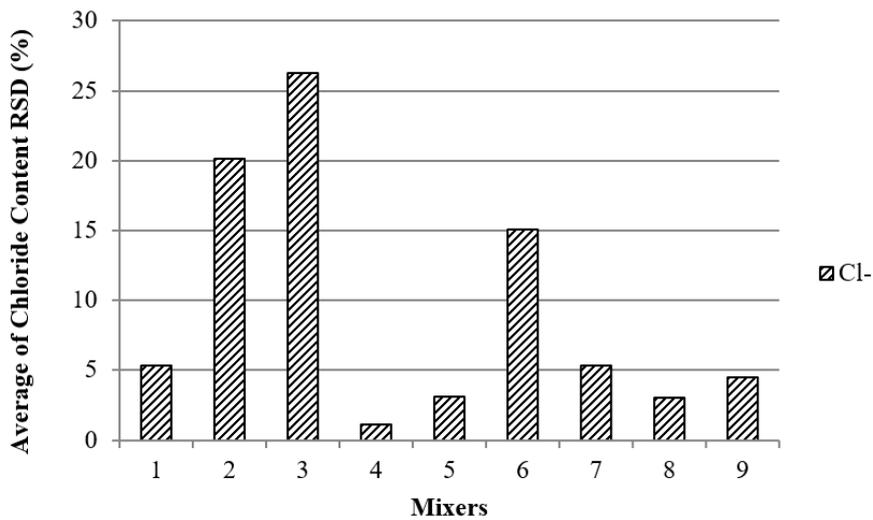


Figure 4: Relative standard deviation of chloride level.

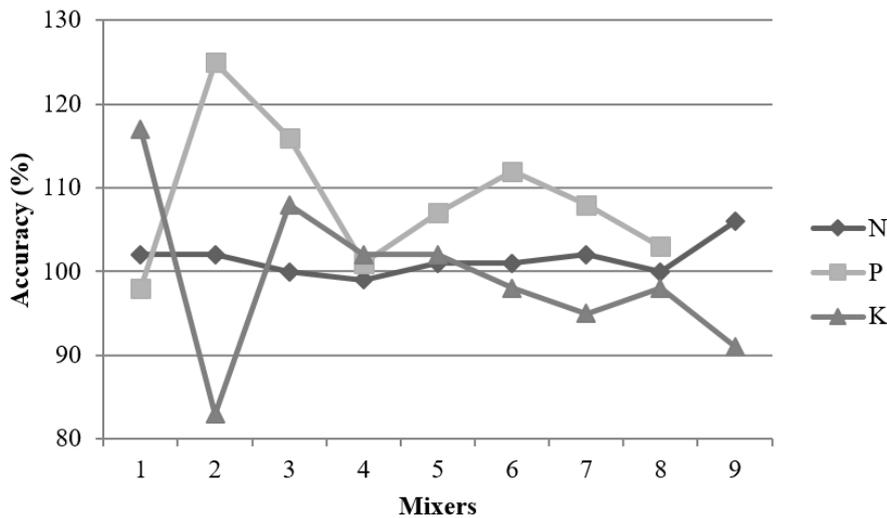


Figure 5: Accuracy of the N-P-K analysis.

ther investigation may be conducted to confirm if there was any problem in raw potash and mixer operation.

P₂O₅ gravimetric analysis takes two full days, costs \$11/sample, and requires \$17,930 in capital equipment. Nitrogen combustion analysis also takes two days, costs \$33,570 for capital equipment and \$0.11 per tested sample. K₂O AA analysis takes 2.5 days with \$55,009 capital equipment cost and \$1.1/sample. In total, the capital equipment cost for N-P-K analysis is \$106,509, \$12.20/sample, and takes up to 6.5 days, as the N-P-K analysis is both a time- and labor-consuming methodology requiring access to expensive instruments. Therefore, a more cost-effective and accurate method to determine blended sample homogeneity and mixer performance would be preferred. Our results also highlight the use of easily identified phosphate fertilizer particles to check homogeneity in certain circumstances. The collected samples consist of three different phosphorous source ingredients: DAP, MAP, and MESZ.

Samples from two cement mixers contained DAP, and samples from the other cement mixer contained MESZ. Samples from the volumetric mixers and two vertical mixers contained MAP whereas samples from the other two vertical mixers contained MAP. The samples from the paddle mixer do not have any phosphorous components (Figure 6). Ten stream samples per mixer were counted for phosphorous source particles, and the percent of relative standard deviation was calculated. The RSDs for each evaluated mixer were 17.1%, 34.8%, 19.7%, 9.6%, 9.7%, 30.2%, 13.6%, and 9.7%.

Although all phosphorous particle counts in evaluated mixers show positive correlations to phosphorous element analysis, only one mixer displayed a strong liner relationship (+0.72); another showed a moderate linear relationship (+0.63), and one had a weak relationship (+0.37). Nevertheless, as mentioned previously, it is possible that the N-P-K ingredient materials broke down, which could have increased the number of par-

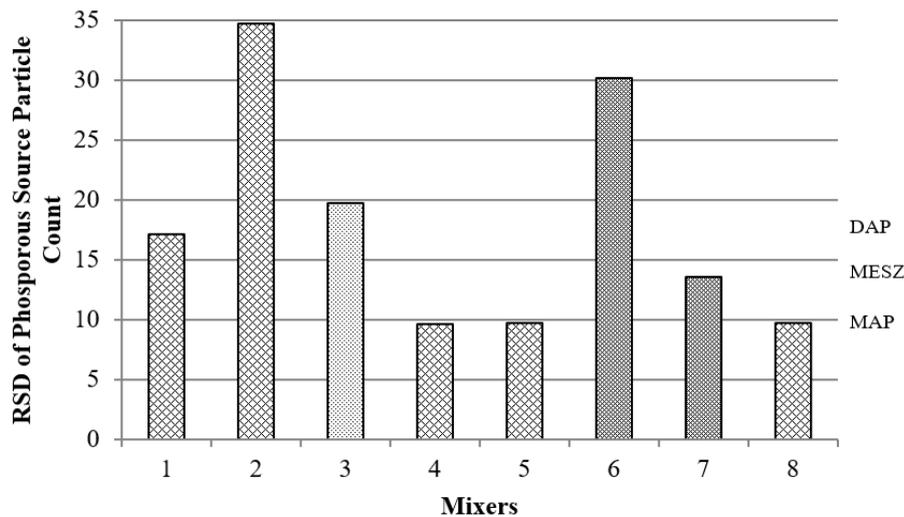


Figure 6: % RSD of phosphorous particle count.

ticles during the blending process and influenced the particle number determination.

Since potassium chloride is a common component of potash, chloride level measurement is an appropriate evaluation method to determine homogeneity and its measures are comparable to that of potassium, as shown by atomic spectrophotometry. In fact, the chloride levels showed a moderate (56%, $n = 5$) to strong (44%, $n = 4$) negative linear relationship to nitrogen analysis. Chloride levels showed a strong negative to strong positive linear relationship to phosphorous in different mixers. In contrast to potassium, two mixers showed perfect (+1.0) positive linear relationship, five mixers showed a strong positive relationship (range from +0.71 to +0.97), and two mixers showed a weaker positive relationship (+0.18) (Figure 7).

The RSDs of potassium and chloride levels for evaluated mixers were also compared. While the RSDs of potassium were calculated as 4.2%, 20.9%, 29.1%, 1.6%, 4.6%, 16.0%, 4.5%, 2.9%, and 3.8%, the RSDs of chloride measurement were 5.3%, 21.1%, 29.3%, 1.1%, 6.6%, 15.1%, 8.1%, 3.0%, and 4.5%, with a +0.99 correlation. Based on these results, chloride level determination proved to be a good method to evaluate homogeneity in fertilizer mixers. The chloride test will provide a result as good as the assay of potassium content (Figure 8). From the potassium and chloride tests, two mixers showed poor performance (>20% RSD), one mixer showed fair performance (15~20%), and 6 mixers had excellent performance (<10%). Both potassium and chloride tests show highly correlated RSD. In addition, the sample preparation and throughput time for the automated chloride titration only takes one day, and costs 10 times less in equipment (\$10,659) and sample testing (\$1.6) compared to N-P-K analysis. A preliminary QuanTab test was previously performed and failed (data not shown) based on the high Cl⁻ content of potash. According to the samples collected from selected mixers, the Cl⁻ content can go up to 19.4%, while the QuanTab high-range chloride testing strip can only detect up to 0.675% Cl⁻ with the original 10 times dilution. In this

study we also compared chloride titration to testing strip. The results from 10 subsamples of one mixer were analyzed using a two-tail paired t-test, with no significant difference. It further indicates that both are good methods to detect chloride in fertilizer. However, it is difficult to weigh precisely and dilute up to 250 times in the field.

5.1. Mixer Evaluation Based on Cl⁻ Determination

Micro-ingredients are generally the materials with $\leq 0.5\%$ of the total contents. Testing mixer performance by a micro-ingredient may provide a better indication of uniformity. However, micro-ingredients are typically more difficult to incorporate into a large batch of fertilizer. Therefore, determination of a common fertilizer component is an alternate and cost-effective method to evaluate sample homogeneity and mixer performance.

Potash ores are typically rich in KCl and sodium chloride (NaCl), and are usually obtained by conventional shaft mining, with the extracted ore ground into granules or powders. There are four common kinds of potash fertilizers: muriate of potash (MOP), sulfate of potash (SOP), potassium magnesium sulfate, and potassium nitrate. Therefore, Cl⁻ from potash was selected to be measured in this study to serve as a good screening method for evaluating homogeneity of fertilizer samples. The percentage of potash was calculated and ranged from 9.0% to 63.9% in the evaluated samples. Next, fertilizer ingredients were blended in the cement mixer for 3 to 6 minutes. Fertilizer samples from vertical mixers were mixed from 12 minutes up to whole loading time. The discharge time for volumetric mixer was 6 minutes and 28 minutes for paddle mixer (Table 4).

Our previous study indicated that mixing time, readiness of the equipment, overfilling, sequence of ingredient, and particle size all result in insufficient blending and segregation [12]. In comparing blending time, our current study indicates that facilities that operate cement mixers have less discharge time than facilities running other type of mixers. In particular, two cement mixers with the highest % RSD in the study have two

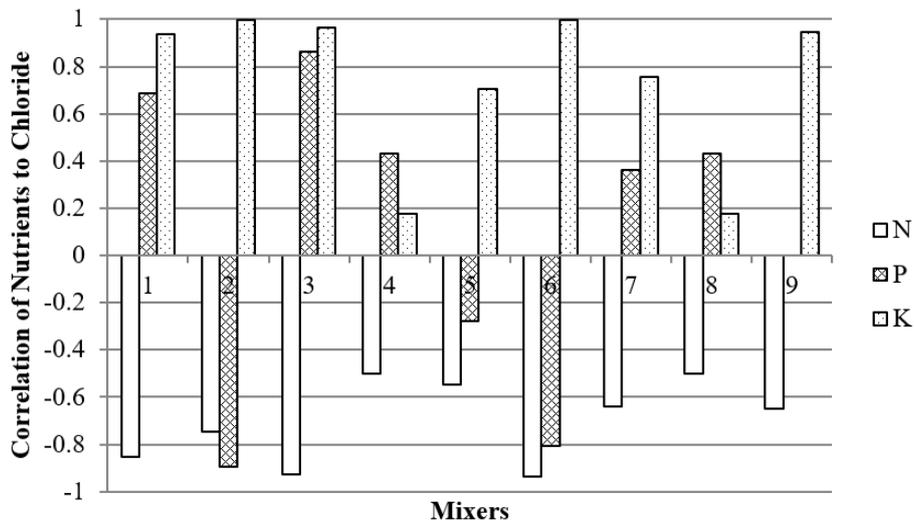


Figure 7: Correlation of N-P-K analysis to chloride level.

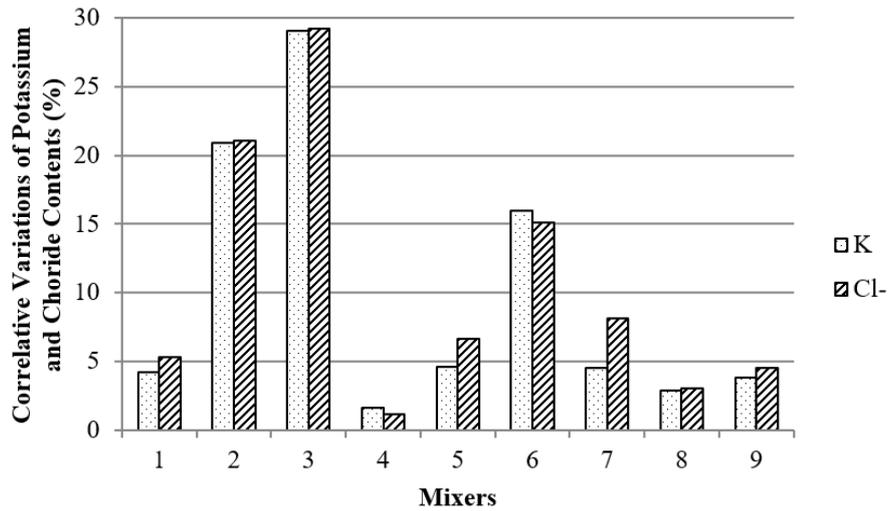


Figure 8: RSDs between potassium and chloride levels

Mixer	Mixing Time	% Potash
#1	4~6	48.4
#2	3~4	33.7
#3	4~4.5	9.0
#4	∞ (mixes as loading the whole time)	22.3
#5	12	34.0
#6	18	15.4
#7	18	15.4
#8	6	13.2
#9	28 (started mixing before truck arrived)	63.9

Table 4: Potash content and discharge time for samples collected from evaluated mixers.

of the lowest mixing times. Based on this finding, a 50% increase in discharge time is suggested to improve performance and achieve better homogeneity.

6. Conclusions

Based on this study, we found that the Quantab chloride testing strip can serve as an easy and rapid screening method

to evaluate fertilizer mixer performance in the field, especially when the manufacturer is interested in comparing performance results from the same mixer to determine optimal mixing time. Comparing the RSDs of titration and QuanTab tests for stream samples of the paddle mixer, chloride titration had a lower variance (0.78) than the QuanTab test (1.97). An f-test showed that the variance of chloride titration and QuanTab is the same. Based on these results, QuanTab testing may be applied in the field, but the method is complicated by the challenges of accurate weight measurement and a high dilution factor. The chloride titration represents the least expensive evaluation method, while the N-P-K analysis is still the best assay in the laboratory. Further investigation remains to be performed on fertilizer produced in cement mixers to clarify if the higher variation found in this study was due to faulty equipment.

7. Declaration of Conflicting Interest

The authors declares no conflict of interest.

8. Acknowledgement

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9. Article Information

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