



Granulated polyhalite fertilizer caking propensity



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ABSTRACT

Most fertilizers have some tendency to form agglomerates (caking) during storage. This caking is usually effected by: chemical composition, particle structure, moisture content hygroscopic properties, mechanical strength, product temperature, storage time and pressure. The aim of this study is to provide fundamental information on the performance of POLY4, a trademarked granulated polyhalite fertilizer by Sirius Minerals Plc, under long term storage as a fertilizer and in NPK blends. Evaluation of POLY4 blends "caking" is proposed using accelerated caking tests. These accelerated caking tests are of short duration and for this reason can be used in fertilizer granulation plants on a quality control basis. Crushing and Dynamic Vapour Sorption (DVS) tests for individual granules, and caking and DVS tests for POLY4 blends were performed to monitor the behaviour of POLY4 within the various blends. The addition of POLY4 to the blends has a positive effect on the blends by reducing the caking tendency. It was also found that the sample with the largest amount of POLY4 (50%) has the largest creep rate value and longest estimated storage time approximately 300 months.

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1. Introduction

Climate change, soil degradation and growing world population are having detrimental effects on food security as availability and nutritional quality of food decreases [1,2]. By 2050, food production (meat, sugarcane/beet, oil crops and cereals) will have to increase by 53% of current output to satisfy global demand [3]. Furthermore, the global arable area available per person for agriculture dropped from 0.36 to 0.2 ha in the last 50 years whilst displacement of edible crops for cash crops widens yield gaps, and lowers food security driving the demand for quality fertilizers to improve food yields [4,5]. As a result of driving demand for food security from smaller areas, fertilizers that deliver nutrients efficiently need to be produced and maintained. Globally, 110.9 million tonnes of nitrogen fertilizer, 41.9 million tonnes of phosphate fertilizer and 31.9 million tonnes of potash fertilizer were demanded in 2014. This is expected to increase by 6.5%, 8.7% and 10.5% for nitrogen, phosphate and potash fertilizer respectively by 2019 [6]. Therefore, more fertilizer products will be needed yet the diversity of products, shown in Table 1, raises challenges of maintaining quality. One of the greatest concerns for a fertilizer manufacturer is its shelf life, which is effected by hygroscopy of the granules that influences caking propensity [7]. Caking of fertilizers is the undesired

agglomeration of granules through the formation of crystal bonds or mobile liquid bridges between the granules [8,9]. All fertilizers are hygroscopic and will absorb moisture above a specific humidity known as the critical relative humidity (CRH). Above the CRH, moisture is absorbed leading to increased caking tendency, which over prolonged exposure can penetrate bulk fertilizers resulting in severe caking [10]. Another challenge with maintaining fertilizer quality is when fertilizers are combined into NPK blends because each fertilizer has a different CRH and caking propensity. Some fertilizers can have limited or no compatibility (e.g. urea and triple super phosphate) with others for safety and chemical reasons [11]. Little data is available on the compatibility of individual and blended fertilizers. Further complications can arise as new fertilizer products, such as polyhalite, are introduced. Polyhalite is an evaporate mineral, formed by successional marine evaporation events throughout history [12]. Polyhalite comprises potassium, magnesium and calcium in the form of sulphates with the chemical formula of $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. The use of polyhalite as a fertilizer was discovered by Fraps and Schmidt in 1932 [13]. By conducting trials in the US on corn and sorghum in both single and multiple croppings, Fraps and Schmidt [13] established the potassium in polyhalite to be a 96% equivalent available compared to muriate of potash (KCl) or sulphate of potash (SOP). The recent assessment by Kemp et al. [12] found that the world's largest highest grade deposit of polyhalite (2660 Mt. at 85.7% grade) is located in North Yorkshire, United Kingdom that has reignited interest in polyhalite as a potassium bearing, low chloride fertilizer. To date, little is known about the physical characteristics of polyhalite for long term storage and use as a fertilizer on its own or in NPK blends. In this paper, the polyhalite used is referred to as POLY4, the trademark

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Table 1
Summary of production processes for a range of N, P and K fertilizers (after refs [17] and [26]).

Nutrient source	Fertilizer product	Chemical formula	Production method
Nitrogen	Ammonia	NH ₃ or NH ₄ OH	Combining N ₂ and H ₂ under high temperature and pressure (Haber-Bosch process). Forms a gas that is compressed into liquid form
	Ammonium sulphate	(NH ₄) ₂ SO ₄	Manufacturing of coal gas or coal coke as a reaction between ammonia and sulphuric acid. Produced as by-product from other industries. Reaction form crystals
	Ammonium nitrate	NH ₄ NO ₃	Combines ammonia gas with nitric acid to form concentrated solution. Granulated via spraying into a rotating drum or hardened into prill in falling tower
	Urea	CO(NH ₂) ₂	Controlled reaction of NH ₃ and CO ₂ under high temperature and pressure. Molten urea is granulated or hardened into prill in falling tower
Phosphorus	Monoammonium phosphate	NH ₄ H ₂ PO ₄	Combines ammonia and phosphoric acid to form a slurry that solidifies in a granulator. Alternatively, pip-cross reactor can be used to generate heat and solidify the slurry
	Diammonium phosphate	(NH ₄) ₂ HPO ₄	Combines ammonia and phosphoric acid in controlled reaction to form hot slurry. Mixture is cooled, granulated and sieved
	Single superphosphate	Ca(H ₂ OP ₄) ₂ ·H ₂ O	Ground phosphate rock and sulphuric acid combined to form semi-solid that is cooled. Material is cured for several weeks to harden. Once hard, material is screened or granulated
	Triple superphosphate	Ca(H ₂ PO ₄) ₃ ·H ₂ O	Ground phosphate rock and phosphoric acid reacted in cone-type mixer or slurry spraying onto a nuclei for during rotating granulation
Potassium	Potassium chloride	KCl	Sylvinite is processed (beneficiated) to remove sodium salts resulting in KCl chips. Hot water injection into sylvinite deposit forms brine that is dried at surface. Alternatively, solar evaporation of brine can occur
	Potassium sulphate	K ₂ SO ₄	Reaction between KCl and sulphuric acid, historically. Washing minerals such as kainite and schoenite removes undesirable products. Chemical separation from potassium magnesium sulphate or polyhalite
	Potassium magnesium sulphate	K ₂ SO ₄ ·2MgSO ₄	Mining of langbeinite that is washed to remove impurities and crushed to desired particle size
	Potassium nitrate	KNO ₃	Reaction of KCl with sodium nitrate, nitric acid or ammonium nitrate to form crystals for dissolving in water or solid prills
	Polyhalite	K ₂ Ca ₂ Mg(SO ₄) ₄ ·2H ₂ O	Mining of polyhalite rock that is crushed and screened into chips, powdered or granulated with a binder

name for Sirius Minerals polyhalite granules. The aim of this study was to understand the storage characteristics of POLY4 as a fertilizer and inclusion in NPK blends. Specifically, the objectives were i) to determine the CRH and caking propensity of POLY4, ii) assess other fertilizers for CRH and caking propensity, iii) assess common NPK blends of fertilizers to determine compatibility and caking propensity.

large number of combinations of fertilizer blends to choose to study, as blends vary with individual crop type, environment used and fertilizer availability. The introduction of POLY4 as a potassium source into blends further increases the number pool of blends to choose from even further. The specific blends chosen here are of industrial interest which allowed us to narrow our focus.

2. Materials & procedures

2.1. Fertilizer blends

All fertilizer granules and POLY4 blends were supplied by Sirius Minerals Plc., United Kingdom and used for the various tests without any modifications. Table 2 shows the compositions of the various blends tested in this study. It is worth mentioning that there is an extremely

2.2. Crushing test

Single granule diametric compression measurements were performed using a TA.XT2i Texture analyser materials testing machine with a PC for real time data logging and analysis. The granule strength was determined from diametric compression of the single granules. The granules were compressed at 1 mm/min between two stainless steel plates. As fertilizer granules have irregular particle sizes and

Table 2
Polyhalite blends as provided by Sirius Minerals Plc.

Sample ID	POLY4	Ammonium nitrate (AN)	Diammonium phosphate (DAP)	Kieserite (KIE)	Ammonium sulphate (AS)	Urea	Calcium phosphate (TSP)	Single Super phosphate (SSP)	Muriate of potash (MOP)	Phosphate rock	Sand
1.	19.5%	47.0%	21.5%	–	–	–	–	–	12.0%	–	–
2.	20.0%	–	21.7%	–	–	35.0%	–	–	12.0%	–	11.3%
3.	–	–	21.7%	–	–	35.0%	–	–	16.7%	–	26.6%
4.	–	40.9%	22.7%	4.8%	14.1%	–	–	–	17.5%	–	–
5.	24.2%	–	43.4%	–	–	4.8%	–	–	27.6%	–	–
6.	13.2%	–	43.4%	1.5%	10.6%	–	–	–	30.6%	–	–
7.	20.3%	6.6%	43.8%	–	–	–	–	–	28.9%	–	–
8.	–	–	–	–	–	21.9%	43.8%	–	33.7%	–	–
9.	20.3%	6.6%	43.8%	–	–	–	–	–	28.9%	–	–
10.	50.0%	–	26.0%	–	–	16.0%	–	–	8.0%	–	–
11.	–	–	41.9%	–	–	25.7%	–	–	32.2%	–	–
12.	20.4%	–	35.4%	–	–	21.7%	–	–	22.5%	–	–
13.	–	–	–	–	–	35.7%	35.5%	–	27.5%	–	–
14.	40.0%	–	17.4%	–	–	28.0%	–	–	4.0%	–	–
15.	–	–	–	–	–	53.1%	26.4%	–	20.5%	–	–
16.	42.0%	–	15.2%	–	–	15.7%	–	–	26.8%	–	–
17.	36.0%	–	8.0%	–	–	17.9%	–	–	26.6%	11.5%	–
18.	45.0%	–	–	13.0%	–	8.7%	30.5%	–	2.8%	–	–
19.	–	–	–	25.0%	–	8.7%	18.5%	34.5%	13.3%	–	–

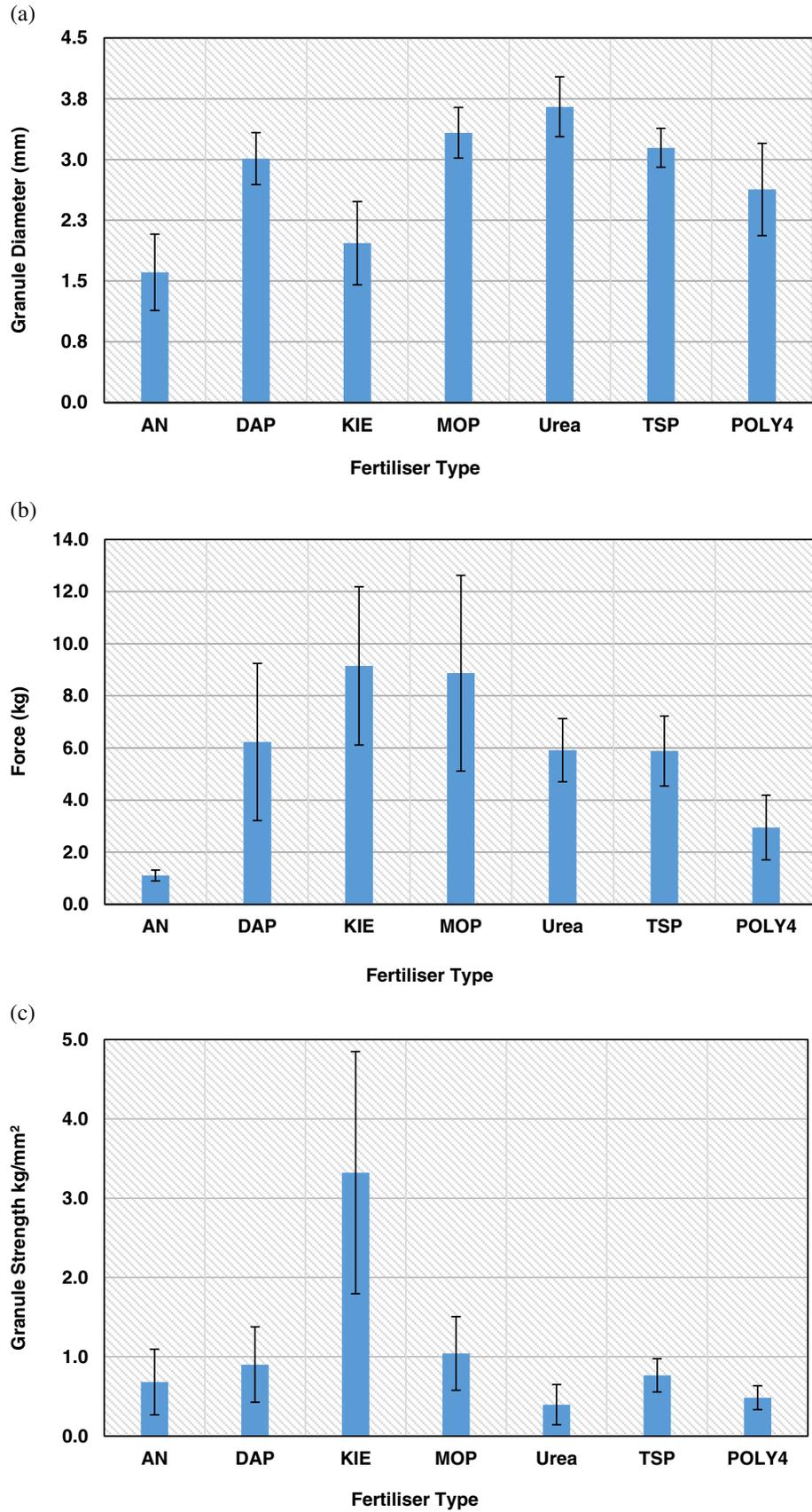


Fig. 1. Results of crushing test for various individual granules indicating granule diameter (a), force to crush a granule (b) and granule strength (c). Granules were provided separately: not from within the blends.

Table 3
Typical crushing strength values (ranges) of some common fertilizers (after [16]).

Fertilizer	Grade	Crushing strength (kg/granule)
Prilled urea	46-0-0	0.8–1.2
Granular urea	46-0-0	1.5–3.5
Granular ammonium sulphate	21-0-0	1.5–2.5
Prilled ammonium nitrate	34-0-0	1.2–1.7
Granular di-ammonium phosphate	18-46-0	3.0–5.0
Granular mono-ammonium phosphate	11-55-0	2.0–3.0
Prilled potassium nitrate	13-0-44	1.5–2.0
Granular potassium chloride	0-0-60	3.0–5.0
Granular potassium sulphate	0-55-0	3.0–4.0

shapes, 20 granules for each fertilizer e.g. POLY4, AN, DAP and MOP were tested to obtain an average [14]. The granule strength was determined using Eq. (1):

$$\sigma = 4 \times \left(\frac{F_f}{\pi D^2} \right) \quad (1)$$

where F_f is the failure load and, D is granule diameter: which is taken as the distance between the platen when first contact is made between the granule and the movable plate.

2.3. Dynamic vapour sorption test

The investigation of sorption properties reported in this study was performed using dynamic vapour sorption (DVS) instrumentation of the type DVS Advantage 2 from Surface Measurement Systems, London, UK. All experiments in this study were performed at 25 °C. A very small

amount of blend is necessary for the sorption experiments; therefore, the different types of granules/blends were ground down to a powder with a maximal particle diameter of 0.5 mm. This does not change the sorption properties of the sample. The sample mass varied between 35 and 75 mg (dry weight). In order for the software to automatically change the surrounding relative humidity (RH) when moisture equilibrium for the sample is obtained, a dm/dt stability criterion must be met (i.e. the sample weight change must be lower than the dm/dt criterion in order to progress to the next %RH value). The dm/dt stability criterion selected for the experiments in the present study was 0.002%/min. The samples were exposed to 0% RH for 5 h and then to 10%, 20%, up to 90% RH for 3 h at each RH values.

2.4. Accelerated caking test

The tests were performed for the blends using a Zwick/Roell Z 0.5 material testing machine with a PC for real time data logging and analysis. A 500 N load cell and a displacement transducer have been used which have resolutions of 0.001 N and 0.23 μm , respectively. A bespoke cylindrical stainless steel die with an internal diameter of 30 mm was used in the accelerated caking tests. The die was filled with a representative sample of granules from each fertilizer blend, consisting of between 18 and 20 g of granules in each test depending on the blend bulk density. The granules were then compressed at loads of 90 psi and the load was then maintained for a predetermined period of 2 h. At the expiration of duration time, the load was then removed. Upon removal of the load, if a cake was formed, the force that is required to eject the cake is then measured. Blends with relatively higher resistances to deformation took longer times to reach 90 psi. On the other hand, shorter times were required for blends with less resistance to deformation/caking. The compact was ejected from the die using the platen, whilst monitoring the force. The maximum force recorded on the load cell just before ejection of the compact was considered to be the ejection force and was used to determine the ejection pressure. The ejection pressure of the cake was used as an indication of the caking propensity of the sample.

2.5. Creep tests

When a constant stress is applied over a period of time to a crystalline material, plastic deformation or creep may occur dependent upon the magnitude of the stress and the time period. The first region of creep is known as “diffusion creep”, where the rate of strain is directly proportional to the applied stress [$\epsilon \propto \sigma$]. A second region is described by “dislocation creep”, whereby the crystals glide over each other under high stress. Dislocation creep is characterized by $\epsilon \propto \sigma^n$ ($n > 1$) [8]. The above information/data was used to calculate the real time storage pressure for the various blends.

3. Results and discussion

3.1. Single granule crushing

The different fertilizer blends that were provided for testing had a wide range of particle sizes and shapes. During the strength measurement, the size of each particle under test was also measure by Texture Analyser Expert. The average particle size of the fertilizer components used in the test are presented in Fig. 1a. Ammonium nitrate (AN) had the smallest particle size in the range of 1.5 ± 0.5 mm and the component with the largest particle size was urea, which was about 3.6 ± 0.5 mm. The size of the Kieserite (KIE) component was around 2 mm and was not statistically different from that of the AN component. Results presented in Fig. 1b show that different components of the fertilizer require different loads to fracture them in the range of 1 kg/granule to 9 kg/granule. These results show that KIE granules required the largest load to crush them, which was around 9 kg/granule. It is also clear

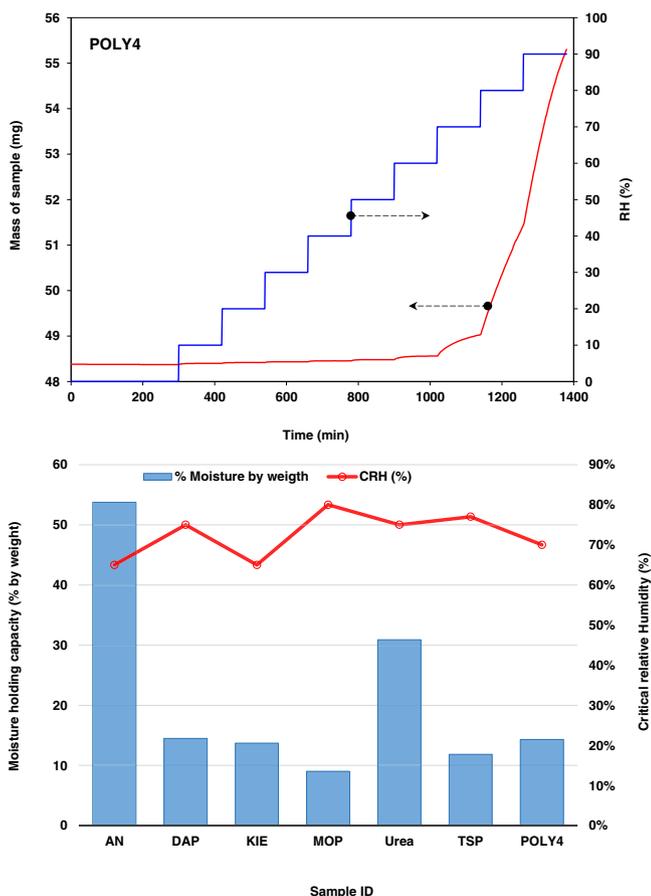


Fig. 2. Results for DVS analysis for POLY4 (as an example), moisture holding capacity and critical relative humidity for the individual components at 25 °C.

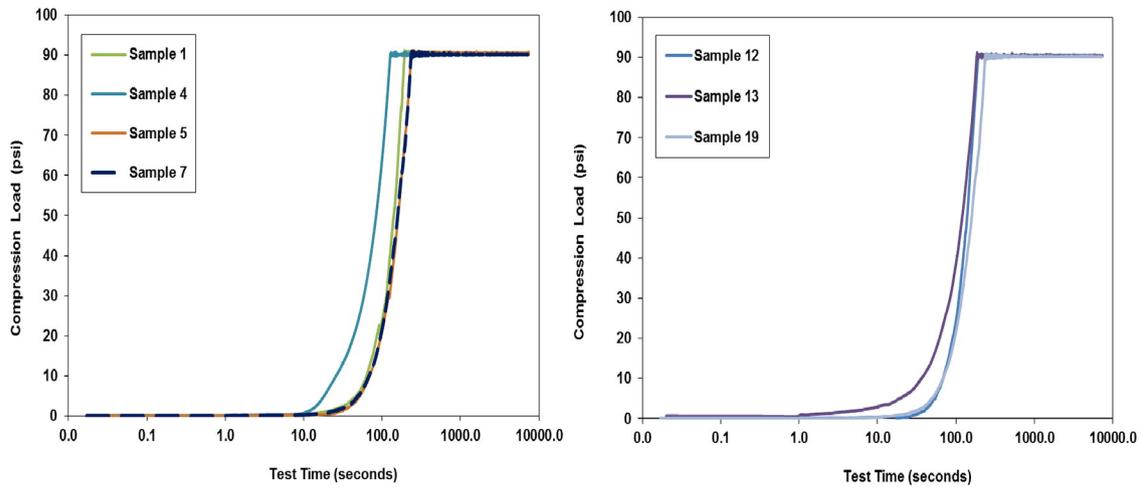


Fig. 3. Compression force profiles for selected samples: 90 psi for 2 h.

that, DAP, KIE and MOP component showed the largest standard deviation in reported failure load values. This could be due to large variation in the size, and shape of particles in these samples. The AN granules were almost spherical hence the least deviation in the reported crushing load values. This variation in granules size may be the cause in the wide range of granule failure load reported for the different types of granules. The particle size difference was eliminated by calculating the nominal strength values which are reported in Fig. 1c. These results show that KIE granules had the strongest granules. High crush strength can be due to fewer irregularities, or fracture propagation points on the granule surface [15]. Overall, all the fertilizer components that were tested had strength values that are comparable to results from literature and sometimes higher than expected, for example the typical strength values for DAP fertilizer was 6.1 kg/granule which is higher than the range 3.4 kg/granule to 4.9 kg/granule [16] for granules in the size range 2.4 to 2.8 mm. Typical strength values for the AN and urea fertilizer granules are in the range 1.2–1.8 kg/granule and 2.0–3.1 kg/granule, respectively, for granules in the size range 2.4 to 2.8 mm. Taking into account the differences in the size ranges of granules used in the test here and the size ranges of the granules reported in literature, the values obtained in the current test are comparable (Table 3) [16,17]. Crush strength is an important characteristic for fertilizer granules to determine suitability for spreading in agricultural spreaders. Low granule strength will lead to

handling issues and upon mechanical spreading some granules would be destroyed before spreading resulting in uneven fertilizer applications. A recommended crush strength of 3 kg/granule is deemed sufficient for spreader use [16]. Although POLY4 granules showed a crush strength of 2.9 kg/granule, spreader testing of POLY4 granules has been conducted by Sirius Minerals showing acceptable spreading patterns [18].

3.2. Single granule DVS

The moisture uptake and CRH results found from the sorption isotherm experiments for the different fertilizers are given in Fig. 2. Also, as an example, the mass as a function of time DVS results for POLY4 is illustrated along with the RH surrounding the sample. The CRH values for the various fertilizers reported in Fig. 2 are very similar to those found in literature [19–21]. It can be seen that water absorption is low at low humidity, however, increases considerably when the CRH is reached at a specific temperature [22]. At humidity values higher than CRH, the fertilizer will absorb moisture from the atmosphere. AN and KIE fertilizers have lower critical relative humidities than other tested fertilizers. The moisture uptake of AS and SSP fertilizers listed in Table 1 have not been tested as they are only used in three blends, however, their CRH values are documented. CRH values for AS and SSP are 75–80 and 80–85, respectively [23]. Also, the amount of moisture absorbed by weight is given in Fig. 2, and it can be seen that AN absorbed the largest amount of water molecules. The order of the fertilizer in terms of the amount of moisture absorbed by weight is AN > urea > POLY4 = DAP > KIE > TSP > MOP. Ammonium nitrate and urea are more hygroscopic than most other fertilizers, and take up moisture from the atmosphere more readily. Coatings are often used, particularly in N fertilizers, to lower the moisture uptake by fertilizer and increase their CRH [10,24, 25]. It can be concluded that, when mixed with other fertilizers, AN and urea may cause some undesirable effects unless coated products are used, (e.g. stickiness which can cause handling difficulties and moisture migration, giving rise to caking tendency).

3.3. Caking test of blends

The compression force profiles for the various blends were recorded during the test and the results for some selected samples are presented in Fig. 3. The figure shows that the different blends have different compression characteristics; different blends required different times to attain the required maximum compression force. In the initial test, the maximum compression pressures were set at 30 and 60 psi and results

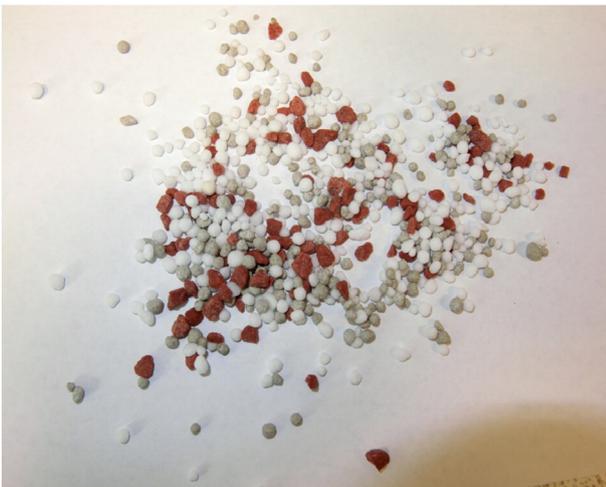


Fig. 4. Image showing the fertilizer granules on removal of the load, after compression to a load of 30 psi – Sample no. 7.

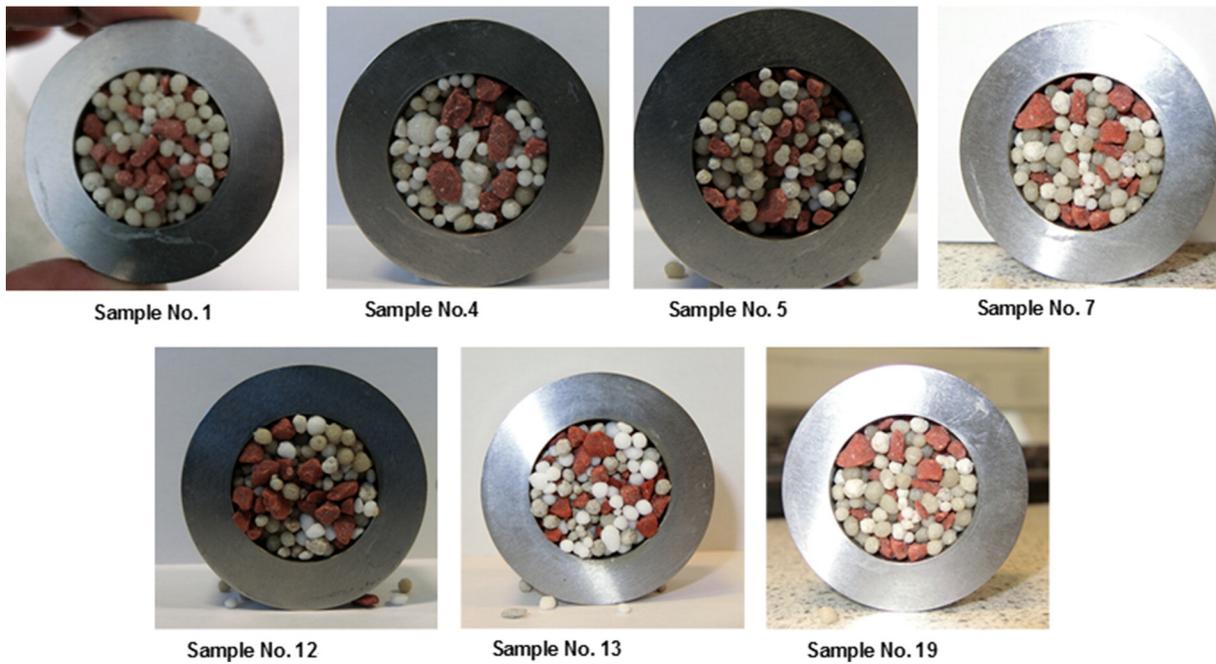


Fig. 5. Images of selected samples after compression to 90 psi for 2 h.

showed that no caking took place, upon removal of the compression load because no bond was formed between the fertilizer granules. The granules collapsed into a loose pile: example shown in Fig. 4. When the compression pressure was increased to 90 psi, caking was observed. On removal of the load at the end of the test, the die could be tilted in a vertical position with minimal granule loss granules on either side of the die (Fig. 5). Generally, for all the samples tested at 90 psi, the compacts remained intact in the die after removal of the compression load showing that caking had occurred. At this compression pressure, a force had to be applied to eject the compact from the die. The maximum force required to eject the compact was recorded for each fertilizer blend and results are shown in Fig. 6. Sample 4, which contains: 40.9% AN 22.7% DAP, 4.8% KIE, 14.1% AS and 17.5% MOP, required the highest ejection pressure. It was interesting to note that of all the tests performed, sample 4 showed the greatest extent of caking. Upon ejection from the die, this sample had the biggest size of compact surviving the ejection. For all the other samples, the compact was reduced to individual fertilizer granules upon ejection from the die. This could be attributed to sample 4 containing AN which has the smallest particle size, lowest CRH, relative weak mechanical strength, and is most hygroscopic. This combination allows AN to act as a sticking agent between the large MOP and DAP

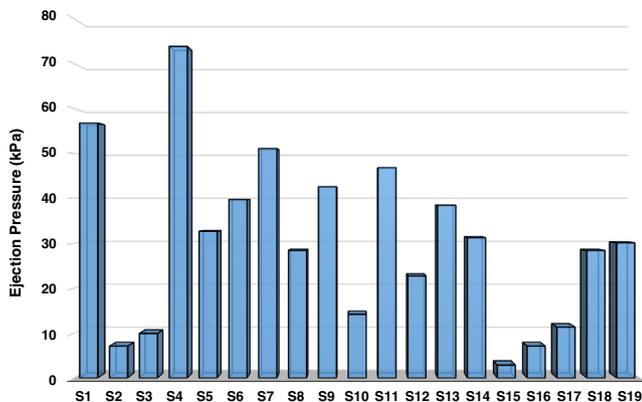


Fig. 6. Ejection pressure for the different samples.

particles and even the very hygroscopic KIE particles. The effect of adding AN on the caking tendency is also seen in samples 1, 7 and 9 although lower due to differences in AN amount and POLY4 inclusion. Sample 15, on the other hand, required the least ejection pressure

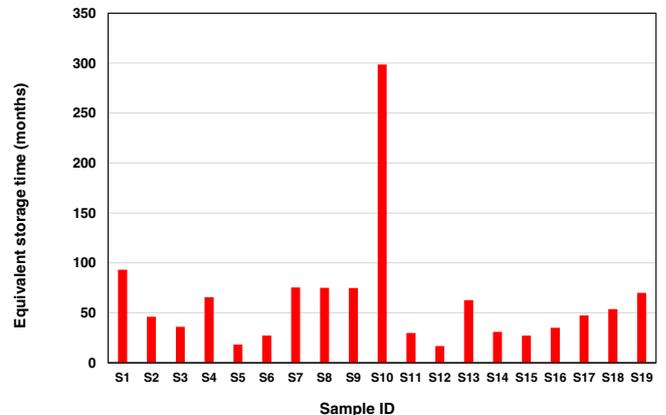
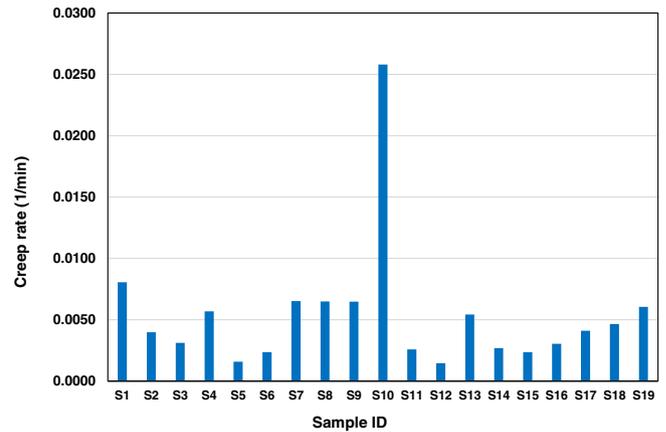


Fig. 7. Creep rates obtained from the strain versus time plots for blend samples during the accelerated caking test and long storage conditions.

(Sample 15 composition: 53.1% urea, 26.4% TSP and 20.5% MOP). This sample contains the granules with the largest sizes and least moisture retaining ability (Figs. 1 & 2). The influence of the particle size and CRH of the individual granules on the caking of the various blends is also observed in samples 2, 3 and 10. These samples are made by combining: POLY4, DAP, MOP and Urea. It can also be observed that the high ability of urea to absorb water is not the main influencing factor on the tendency of caking. Increasing the amount of POLY4 to the blends has a positive effect on the blends by reducing the caking tendency. This can be clearly seen in samples 5, 6 and 7; samples 10 and 11 and samples 16 and 17.

The compatibility of individual fertilizers in a blend determines their caking propensity. Existing matrices [11,26] highlight the compatibility of different fertilizers for existing materials based on CRH and chemical safety. Some fertilizers like AN and MOP are identified as having limited compatibility and would thus have a negative impact on a blend like in sample 4.

3.4. Creep tests and equivalent storage time

By comparison of the creep rates, accelerated caking tests can be modified by varying applied stress and/or time to determine the condition of a fertilizer sample at some future date. In order to calculate the storage time for the various blends in this study, the determined creep rate in the work carried out by Walker et al. [8] for NPK fertilizers, 2.40×10^{-7} , was used. The creep rates and long term storage values calculated for the various blends are shown in Fig. 7. For example, the condition of sample 10 after 2 h at 90 psi equates to $4.30 \times 10^{-4} \times 2 \text{ h} / 2.40 \times 10^{-7} = 214.990 \text{ h}$ (approx. 300 months). Sample 10 which contains the largest amount of POLY4 (50.0%) has the largest creep rate value and longest storage time. This confirms the conclusions obtained in the caking test section [18,27].

4. Conclusions

POLY4 fertilizer blends storage characteristics were assessed to determine the viability of POLY4 in storage and used in NPK blends. Assessment of crush strength identified POLY4 to be of sufficient strength for practical handling and agricultural spreading. DVS testing identified that POLY4 has a CRH of 70%, which was deemed acceptable similar to other fertilizers. Coatings might improve this result although POLY4 had a higher CRH than some coated fertilizers. Accelerated caking tests of 19 blends identified that AN fertilizers often caused caking within blends. POLY4 had no negative effect on NPK blend caking propensity. Creep testing to estimate storage life identified NPK blends with POLY4 had longer storage estimates. Further testing is required to determine the CRH and caking propensity of POLY4 with individual fertilizer granules.

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