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The Investigation 0f Physical Properties of Composite Fertilizer Including Boron Micro Element

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Abstract

Fertilization is one of the most common applications in agricultural fields for achieving high yield. Fertilizer is the important input of agriculture. Raw material costs are nearly 80% of the production costs in chemical fertilizers. Because of high prices, fertilizer usage has started to decrease. The utilization of industrial wastes in the production reduces the costs. Not only is fertilizer expenditure significant, but also the physical properties should be considered. In this study, the physical characteristics of composited fertilizer containing boron which was obtained from the reaction between the diammonium phosphate and borogysum industrial waste were examined. Under laboratory conditions, diammonium phosphate was composited with borogysum at the mole ratio of 1:1 and during this process, the solid/liquid (S/L) ratio, temperature, time, pH of the pulp and speed were 1/3, 40°C, 90 min, 5.5 and 500 rpm respectively. The moisture content, grain (granule) size, tight and loose volume weights, granular fracture resistance and the agglomeration angle of the new product including boron were evaluated. As a consequence, the grain size was in range of 3 and 4 mm, loose volume weight was 1363.32 kg/m^3, the granular fracture resistance was 2.92 kg/granule, agglomeration angle was 89.9 kg/granule and Granulometric Spread Index (GSI) and Uniformity Index (UI) were recorded as 16 and 76.9. These findings were compatible with National and International Standards.

Keywords: Borogypsum, ammonium sulfate fertilizer, physico-mechanical properties of fertilizer, ındustrial waste

1. INTRODUCTION

Recently, the global population has started to increase enormously and thus, the usage of composited fertilizers in agricultural areas has gained importance in order to raise production yields. Both conducting development studies about effective and proper use of fertilizers and the utilization of them which contain macro and micro elements together, play a significant role in supplying nutritional requirements of increasing population. The soil properties, food stuffs in soil, plant types, climate, application procedures and so on should be known for achieving the desired yield from fertilizer [1-2].

The macro and micro nutrition elements are needed for plant growth and boron is one of the crucial micro substances. Boron is a structural mineral which acts as cement and helps consolidate the plant wall [3-4]. Related

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semimetal has influences on fruit and seed formations rather than leaf and shoot. Plant diseases and reductions in plant yields could be appeared in the lack of boron [5]. Besides, it decreases the occurrence of empty fruit in cherry [6], boron is useful in enhancing the nicotine amount of tobacco [7]. Increasing pollination, fruit yields and fruit sets are observed in plant areas where the fertilizer with boron is used [8]. Boron fertilizer is applied to soil and plant leaves. Considering plant types and soil properties, 50-400 g boron is suggested per decare of field [9]. The concentration of solution that will be given to soil ought not to exceed 0.5% [8]. The impact factors on plant beneficialness are pH and organic molecule content of soil and washing and climate conditions. Hence, the application of boron fertilizer to leaves in growing period is proposed thrice [8]. In Turkey, soil analysis were conducted by Soil, Fertilizer and Water Resources Central Research Institute and the boron amounts were declared as insufficient, sufficient, much and excessive in the 46.2%, 31.1%, 19.4% and 3.3% of our country respectively. The insufficient level of boron was reported in 33.72% of Black sea region [10]. Borax decahydrate, sodium pentaborate, disodium octaborate, anhydrous borax and borax pentahydrate are fertilizers for eliminating boron absence in Turkey. But, aforementioned fertilizers are not economic, thus composited ones which involves boron are more suitable [11-12]. Boric acid, which is produced in our country by the General Directorate of Eti Maden Enterprises, is produced because of the reaction of colemanite with sulfuric acid. As can be seen from the equation below, boric acid and gypsum are formed as a result of the reaction [13].

$$Ca_2B_6O_{11}.5H_2O + 2H_2SO_4 + 6H_2O \rightarrow 6H_3BO_3 + 2CaSO_4.2H_2O \quad (1)$$

Due to its very low solubility, $CaSO_4.2H_2O$ (gypsum) is easily separated from the solution and boric acid is crystallized from the remaining solution.

Environmental problems that occur during the operation of mineral deposits in Turkey are storage problems caused by air, soil, water pollution and increasing wastes [14]. In the USA, the precautions to be taken to minimize the negative effects of the wastes generated during the operation of boron mines on the environment are a priority study [15].

Environmental problems caused by pollution are one of the most important problems affecting the progress and growth of mining in our country. Therefore, there are limitations imposed by various standards, regulations, and laws in order to dispose wastes and minimize their damage to the environment [16-17].

During the annual production of 385 thousand tons of boric acid in Turkey, approximately 1155 thousand tons of borogypsum is formed [11].

The usability of borogysum in the production of diamonnium phosphate was investigated in line with this purpose and composited fertilizer containing 0.75% boron was manufactured [18].

On the other hand, physical features of fertilizer are substantial and parameters like sprinkling fertilizer onto soil and storage and delivering of it are critical in the application technique [19-20]. The physical properties are also strictly contributed to the design of fertilizing machines and their settings [21]. Hence, the conformity to National and International Standards of newly formulated products or previous solid mineral fertilizers whose composition was changed, should be checked carefully.

The aim of this research was to analyze the physical specialties of composited fertilizer consisted of plant nutrients and boron which was procured from borogysum. The tight and loose volume weights, grain (granule) size, granular fracture resistance, dimensional analysis and the agglomeration angle were the parameters evaluated. The compatibility of data to TS 2832 Fertilizer Regulation was also checked. It is thought that, this study which scrutinizes the valuable methods and devices in determining the quality indices of a composited fertilizer, will be a guide for scientists and engineers.

2. EXPERIMENTAL

2.1. Material and methods

As a raw material, borogysum was used which was supplied from Eti Holding, Solid Waste Facility of Emet Boric Acid Fabric, Kütahya Moist borogysum was waited at room conditions firstly and then dried at 100°C in an oven (Gemo DT104), until no weight changes were observed. Dried sample was subjected to both particle and composition analysis and 100 mesh size (under sieve) of borogysum was utilized.

Table 1 and Figure 1 represent the chemical composition and X-ray diffractograme of borogysum respectively. Chemical composition was revealed by ICP-MS (Spectro blue ICPOS) and the brand of X-ray diffraction was XRD-Rigaku Smartlab.

Table 1 Chemical constituents of borogysum

Compound	Composition(%)*
B_2O_3	6.52
SiO_2	7.14
SO_3	43.40
CaO	26.38
MgO	1.15
Fe_2O_3	0.72
Al_2O_3	0.83
Na_2O	0.16
SrO	0.95
As_2O_3	0.15
H_2O	12.60

*percentage by weight

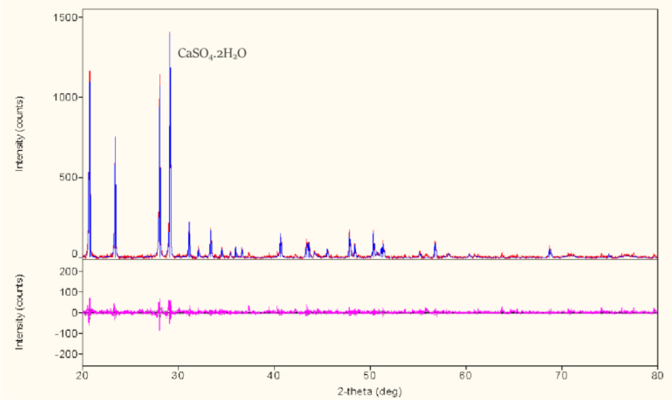

Figure 1 X-ray diffractograme of raw material

Diammonium phosphate (DAP) (contained 46% of P_2O_5, 18% N) was obtained from Apaydın Fertilizer Fabric, Osmaniye.

DAP was put into a 1 L reactor (Dragonlab OS20-S) with a mechanical mixer and water was added into medium keeping the solid/liquid rate of 1:3. Heating was applied to 40°C. After that, DAP was composited with borogysum at equal moles and mixing process was continued. Time, pH of the pulp and mixing speed were 90 min, 5.5 and 500 rpm respectively. Finally, the temperature of the product was kept at 90-100°C in the oven (Gemo DT104) for 2-3 hours.

2.1.1. The determination of grain (granule) size (Screening test)

Particle size is an important factor in the usage of fertilizer distribution machines and packaging. Furthermore, particle size has an impact on the style of fertilizer sprinkling in related equipments. Trials were performed according to TSE EN 1235 standard by using a mechanical screening machine including a sieve set. Several measurement techniques are available in specifying the particle sizes and their distributions. Generally, particle size is reported by means of an average particle size (d_{50}) or a particle guide number (PGN). When d_{50} is multiplied with 100, PGN value is obtained. For instance, a fertilizer whose d_{50} value is 2.5, has a PGN of 250 [22].

The distribution of particle size could be expressed as either Granulometric Spread Index (GSI) or Uniformity Index (UI). Some companies may give both of them in specification forms. GSI and UI enable to test the distribution of diameter size as shown in Figure 2. Information and mathematical expressions which are useful for calculations are given in the following;

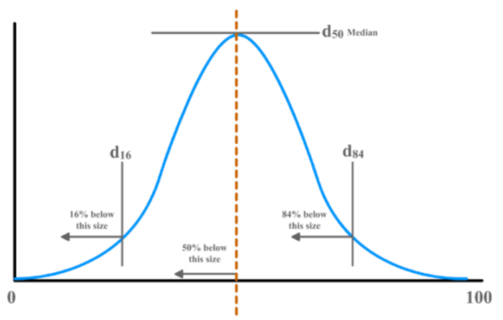

Figure 2 Particle size distribution that demonstrates d16, d_{50} and d_{84} for a fertilizer sample [22]

d_{50} value could be identified with the aid of GSI (Equation 2) [23-24], UI (Equation 3) [21] or screening analysis.

$$\text{GSI} = \frac{(d_{84}-d_{16})}{2 \times d_{50}} \times 100 \qquad (2)$$

$$\text{UI} = \frac{d_{95}}{d_{50}} \times 100 \qquad (3)$$

2.1.2. The determination of loose volume weight

This test is based on measuring the weight of fertilizer which is transferred from a standard funnel to a graduated cylinder (Equation 4) (TS 3740 EN 1236-1,Fig 3,[25]).

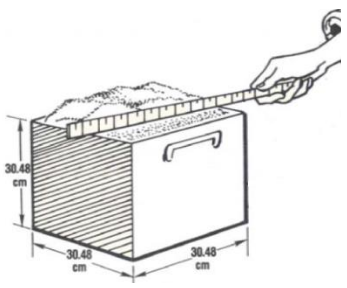

Figure 3 Equipment used tofind the heap angle of fertlizer

$$\rho = \frac{\text{LW}}{\text{V}} \qquad (4)$$

ρ : Loose volume weight (kg/m^3)

LW : The weight of sample (kg)

V : The brimming volume of graduated cylinder (m^3)

2.1.3. The determination of tight volume weight

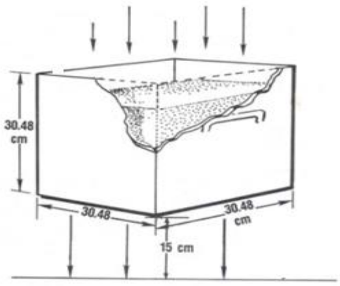

Figure 4 Compacted volume weight measurement (Box volume 0,0283 m^3)

Tight volume weight is described as the weight of any material per unit volume, after filling it to a container and pressing under specific conditions (Fig 4). This parameter is usually stated as kg/m^3 (TS 6801 TSEN 1237). While measuring, fertilizer is piled into a can up to the brim and a linear ruler is used for slipping excessive amounts on the top. Then, can is thrown from a height of 15 cm to the concrete floor, so the sample in the can is able to be pressed. Failing amount in the can is fulfilled, slipped and thrown from the same height again until pressing process is completed. Equation 5 is valid for calculating tight volume weight.

$$\rho_L = \frac{\text{SW}}{\text{V}} \qquad (5)$$

ρ_L : Tight volume weight (kg/m^3)

SW : The weight of pressed sample (kg)

V : The brimming volume of graduated cylinder (m^3)

2.1.4. The specification of agglomeration angle

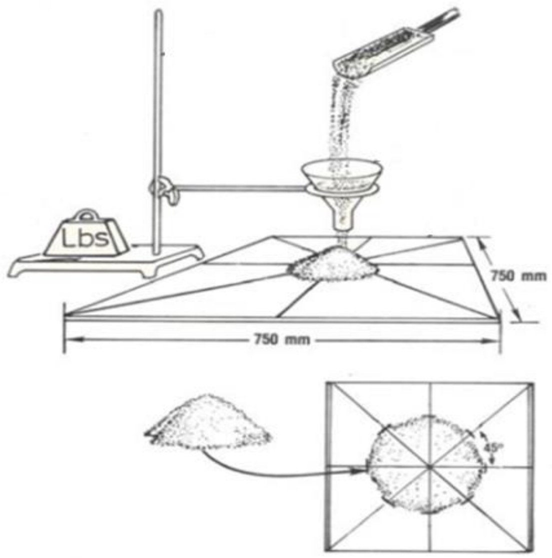

Figure 5 Equipment used to find the heap angle of fertilizer

The stacking angle, is calculated from equation 6 in degrees, [23-25](Fig 5).

$$\alpha = \arctan \frac{2h}{d-d_i} \qquad (6)$$

h : The height of cone (mm). 120 mm is a generally accepted value.

d : The arithmetic mean of measured four diameters which form right angles of 90 degrees each other at the bottom (mm)

d_i : The outlet diameter of funnel (25 mm)

2.1.5. The specification of granular fracture resistance

At least, 25 pieces of fertilizer granule are broken by hardness measurement device (Chaltion measuring ınstrument) and results are recorded [1].

2.1.6. The specification of moisture content

Moisture analysis was conducted according to TS 2832-1 (Equation 7).

$$M = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \qquad (7)$$

M: Moisture level (%)

m_1: The mass of empty container (g)

m_2: Total mass of empty container and initial sample (g)

m_3: Total mass of empty container and dried sample (g)

3. RESULTS AND DISCUSSION

Nine sieves calibrated previously were used for screening analysis and average diameter (d_{50}) was calculated. Granulometric distribution is given with GSI and the mean diameters of fertilizers usually change between 2.5 and 4.5 mm [26]. Figure 6 depicts the results of screening test and it can be inferred from the figure that the average diameters are in range of 3 and 4 mm.

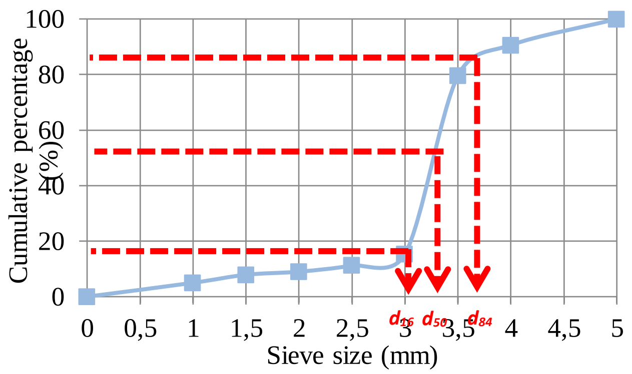

Figure 6 Granulometric distribution of composited fertilizer produced from borogysum

During the formation of composited fertilizer, the effect of washing process were also assessed. The unwashed and washed were composited fertilizer evaluated with scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX). The SEM images shows the surface morphology of the composited fertilizer as shown in Fig.7a and 7c, respectively. The grain sizes are still in good agreements with the granulometric distribution. The EDX analysis show that after washing process Nitrogen (N) peak was disappeared which is due to water solubility of Ammonium Sulfate ($(NH_4)_2SO_4$).

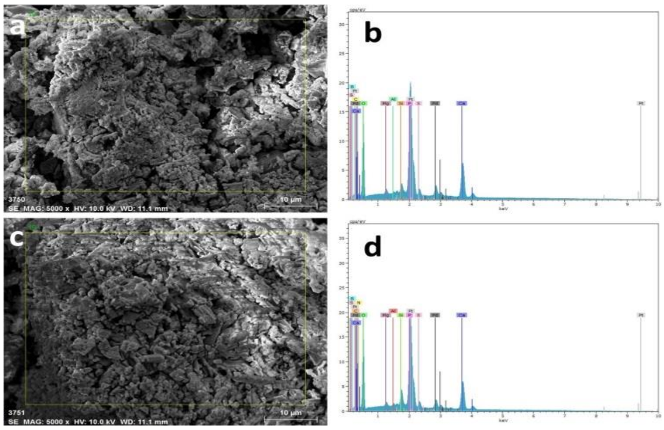

Figure 7 Scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) analysis of composited fertilizer produced from borogysum after (a, b) and before (c, d) washing step

Table 2 expressed the chemical properties of DAP and composited fertilizer and the contents of nitrogen and phosphor in new product were lower than DAP. On the contrary, boron, sulphur and calcium were only detected in aforementioned fertilizer. The quantities of total plant nutrients were close to each other in both of them, but the level of these elements in composited one, were a bit higher than the commercial. It is thought that, this will contribute the effectiveness of new fertilizer positively. Same results were reported by [27] in the production of triple superphosphate with borogysum.

Table 2 The moisture, mineral and phosphorus pentoxide amounts of fertilizers

	DAP	**Composited Fertilizer**
Moisture (%)	1.5	0.80
Nitrogen (%)	$18_{-1.1}$	12.84
Phosphor (%)	$46_{-1.1}$	31.40
Sulphur (%)	-	10.22
Boron (%)	-	0.47
Calcium (%)	-	10.15
P_2O_5 soluble in water and neutral ammonium citrate	$46_{-1.1}$	31.40

The tight and loose volume weights of fertilizers with and without borogysum were calculated as 1370.87, 1363.32 kg/m^3 and 1258.23, 1253.43 kg/m^3 respectively (Table 3). As is known, having high density makes the shipping of a product easier and correspondingly, the transportation costs reduce. When considered from this point of view, novel product has an advantage. Moreover, volume weights are directly related to the spreading width of fertilizer machine. Because, granules owning high densities are able to spread on a large area and dust particles do not occur at high rates of rotating discs [28]. As GSI value is low and UI is high, so the particles of fertilizer are smooth and homogenous, and hence uniform spreading is ensured.

Table 3 The physical qualifications of commercial and new products

	DAP	**Composited Fertilizer**	**Aim**
Particle size (%, 1-4 mm)	Minimum 90	91	Ensuringeffective use of fertilizer distribution machines
Particle size (%, 1 mm, under sieve)	Maximum 3	3	Ensuring proper storage of fertilizer
Loose volume weight (kg/m^3)	1253.43	1363.32	Ensuring proper storage and transportation of manure
Tight volume weight (kg/m^3)	1258.23	1370.87	To prevent slipping in the storage area
Agglomeration angle (°)	89.91	89.55	Determine granule resistance
Granular fracture resistance (kg/granule)	2.92	2.85	Keeping the fertilizer in granular form
GSI	16.00	17.60	Granulometric Spread Index
UI	76.90	75.00	Uniformity Index

Granular fracture resistance is defined as the resistance of granules against deformation or fraction under pressure. Fracture resistance is useful for designating pressure boundaries during fertilizing, transport and delivering facilities of granule material which can be attributed to the particle volume weight and size. If a substance has a low fracture resistance, aforementioned operations will cause negative effects on granules and thus, they will be crashed and converted into dust.

4. CONCLUSION

The physical as well as chemical properties of fertilizers in agriculture are significant. The factors which have enhancing effects on fertilizer costs are the high price of raw materials and being imported from abroad. For this reason, local raw materials could be an alternative. The usage of borogysum, a material which comes out as a result of boric acid production in fertilizer manufacturing, reduce dramatically the waste storage costs and environmental pollution. High nutritional value for plants in this newly formed product is another key parameter.

In this study, a previously obtained composited fertilizer [10] which included boron, phosphor, sulphur and calcium together was developed and the physical quality indices were evaluated. At the same time, a commercial sample was compared with newly formed product and advantages and disadvantages were clearly revealed. The utility of composited fertilizer in cultivated areas were investigated as well as a consequence, fertilizer with boron is superior and could be preferable in fertilizer production. Being compatible to national and international standards will step forward this fertilizer in the market.

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