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Flue Gas Desulfurization Products Use on Agricultural Land Use Systems

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Review Article

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ABSTRACT

The Flue gas desulfurization (FGD) process is a set of technology that is used to remove the sulphur dioxide (SO_2) present in the flue gas, which is exhausted from the thermal power plant during electricity generation. In FGD equipment, high calcium-containing sorbent materials are sprayed, which will react with the SO_2 present in the flue gas and result in the formation of calcium sulphite and FGD gypsum *etc.* these formed waste materials are known as FGD products. The FGD products can be used in agricultural land for the amelioration of the soil acidity, salinity and alkalinity, it improves the soil's physical property, reduce the runoff rate *etc.* Now a day around two per cent of generated FGD products is used in the agricultural field. As some of the FGD products may contain heavy metals, their direct use in the agriculture field may cause environmental hazards. To avoid environmental pollution before its direct use the chemical properties of the product have to be thoroughly checked. So by the use of these materials in the agricultural field, we can effectively convert waste material into useful products.

Keywords: Flue gas; sulphur dioxide; flue gas desulphurization; FGD gypsum; FGD products.

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1. INTRODUCTION

For the production of electricity, we have many alternatives one among them is the combustion of coal products. But enormous volumes of byproducts are produced during coal burning, which are referred to as coal combustion products (CCPs) [1]. It is the richest source of minerals and is considered the third-largest mineral resource in the world [2]. Based on the generation, and characteristics these CCPs are classified into four groups such as fly ash, bottom ash, boiler slag and flue gas desulphurization products (FGDs) [2]. Among these fly ash production rates is very high around 50 per cent of total CCPs, followed by FGDs (24%) [1].

Flue gas desulphurization is an emerging technology, that is used to remove the Sulphur dioxide (SO_2) gas present in the fumes of burning coals, using a high-calcium sorbent material like lime or limestone [3]. While burning coal products higher amount of fumes will be generated when these fumes are emitted through the thermal power plant chimney then which is called flue gas. When SO_2 is removed from that flue gas then that process is known as flue gas desulphurization. If we are not removing the SO_2 from the fumes it will be directly emitted into the atmosphere from there SO_2 will react with atmospheric oxygen and result in the formation of Sulphur trioxide [4]. Once this Sulphur trioxide reacts with the vapor molecule it will result in the generation of sulphuric acid [5]. The sulphuric acid reaction with rainwater results in the generation of acid rain [6]. So in order to reduce the generation of acid rain it is very essential to remove the SO_2 present in the flue gas. So in thermal power stations installation of FGD equipment (Fig. 1) is inevitable. A number of SO_2 control technologies are in use, while others are in different stages of development. Commercialized methods include wet, semi-dry (slurry spray with drying), and entirely dry processes [7].

FGD equipment has to be installed before the chimney of the thermal power plant. Flue gas will enter the equipment through the inlet fleabag and above the equipment it contains a perforation area it is nothing but the atomizer. This atomizer sprays high calcium sorbent material such as limestone, calcium oxide or calcium hydroxide. These high calcium sorbent materials react with the SO_2 and remove them from the flue gas. So the flue gas which is coming out of the equipment will be free of SO_2 gas. Hence to a great extent, the generation of acid rain can be reduced. When the high calcium sorbent materials like limestone or calcium oxide react with SO_2 it will form FGD products. FGD products based on their generation are of three types such as non-stabilized FGD products, stabilized FGD products and oxidized FGD products [8]. The first products formed through FGD products are non-stabilized FGD products. That calcium carbonate reacts with SO_2 in flue gas and results in the formation of calcium sulphite hemihydrate ($CaSO_4 . \frac{1}{2} H_2O$) (Fig. 2).

$$CaCO_3 + SO_2 = CaSO_4 . \tfrac{1}{2} H_2O$$

Calcium carbonate + Flue Gas = Calcium sulphite hemihydrate

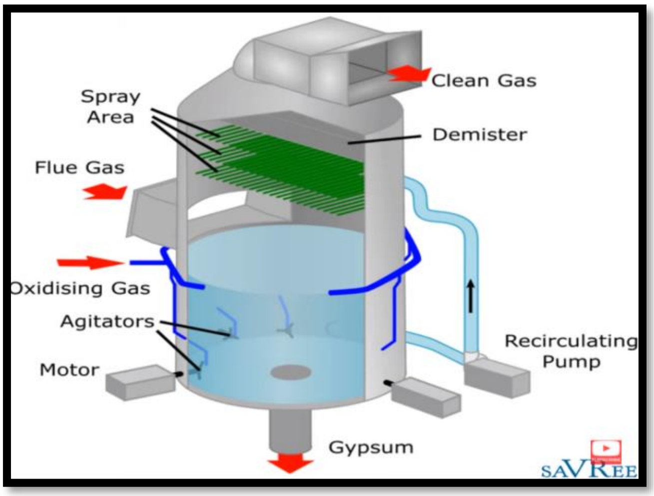

Fig. 1. Flue gas desulphurization equipment

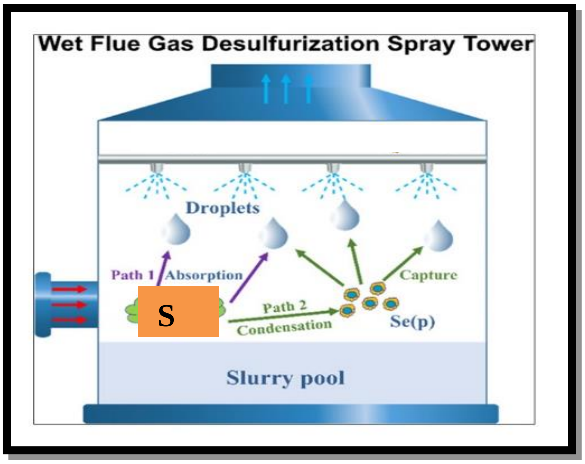

Fig. 2. Non-stabilized FGD products

The formed calcium sulphite is a slurry pool, which is very difficult to handle. So some advanced technology has to be used. The forced oxidation reaction is one of the technology, in which using some agitator oxygen gas externally is provided into the equipment. The given oxygen will react with the slurry pool and result in the formation of FGD gypsum [2]. Instead of giving oxygen, we can also provide fly ash or calcium carbonate or calcium hydroxide, thus formed products are known as stabilized FGD products. While comparing the properties of these three products it was found that three of the products contains plant essential nutrients in comparable amount. But the heavy metal concentration status is low in oxidized FGD products than that of others [9]. So scientists are recommending oxidized FGD gypsum in the agriculture field in order to reduce heavy metal toxicity in soil. FGD products generation and their use get increased from the year 2006 to 2016 [10]. The main FGD products marketing area is located in the Asia continent [11]. Out of the total generation, around 80 per cent are used for construction purpose, and 10 per cent is used for cement preparation. In the agriculture field, two per cent of the total generation is using.

While we are using FGD products in the agriculture field we have to check the nutrient status of the FGD products. It is better to use FGD gypsum in agriculture than other products, so the heavy metal toxicity can be reduced to a greater extent. Actually, these FGD gypsum is not a waste product if we are using it in a scientific way in our field so we can say that it is a resource rather than a waste. The main benefits which we will get with the use of these FGD products are mentioned below.

2. AMELIORATION OF SURFACE AND SUBSOIL ACIDITY

When we use FGD products in agricultural land for surface acidity amelioration, it should contain more unspent calcium hydroxide. Then the calcium hydroxide in the FGD products will ameliorate the soil acidity better than that of the normal agriculture lime why because the calcium carbonate equivalent of CaOH is higher than that of $CaCO_3$ [12]. Similar results were obtained in one experiment which was conducted by Chen et al. [13]. From the experiment, they could find that at the 2nd and 20th months after the application of FGD products in the acidic soil, the soil pH increased from 4.5 to the neutral range. The FGD products used plots show better soil pH than that of the control plots and agriculture lime used plots. From this study, they could also find that is alfalfa crop grown in the FGD products used plots show increased biomass weight than that of the control plots. The reason is that alfalfa could perform in better way when soil acidity gets improved. Alfalfa performance was better in FGD products used plots than that of agriculture lime used condition. Here FGD products ameliorate the soil in a better way than that of the agriculture used condition, than amelioration FGD products also provide some nutrients to the soil which also helped for the improved performance of the alfalfa crops. Zhou et al. [12] found that the breakdown of applied FGD gypsum in a West Virginia acidic Gilpin silt loam soil dramatically enhanced exchangeable Ca and Mg while decreasing exchangeable Al in the top 0-15 cm soil profile, resulting in a rise in soil pH. In this study, the mobility of Ca and Mg through the soil profile was due to the presence of S in the FGD.

To reduce subsoil acidity, we must utilize FGD gypsum instead of FGD products with higher CaOH levels. After applying the FGD gypsum, it must be well mixed with the soil before flooding [14]. Whatever $CaSO_4$ is present in the FGD products will quickly dissolve in water. Ca^{2+} and $SO_4{}^{2-}$ ions will migrate to the subsurface area of the profile with the percolating water. Ca^{2+} ions from the subsurface may replace H^+ ions, causing the soil pH to rise (Korcak *et al.,* 1998). FGD gypsum is superior to $CaCO_3$ for subsoil acidity mitigation because, unlike $CaSO_4$, $CaCO_3$ is less soluble in water, preventing Ca ions from reaching the subsurface region and hindering adequate amelioration.

3. AMELIORATION OF SODIC SOIL

For the amelioration of soil sodicity, FGD products can be used. But before selecting the FGD products we should check the chemical nature of the products. For sodicity amelioration, the products should have a larger amount of gypsum*, i.e.*, FGD gypsum is preferable for soil sodicity amelioration. Following the application of FGD gypsum, the area should be thoroughly irrigated [15]. The Ca^{2+} ions present in the FGD gypsum will replace the Na^+ from the exchange site of the soil. Then the soil pH, soil exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR) get reduced to normal value. In one field study, Zaho and his coworkers in 2018 could find the same result, when they applied FGD gypsum to the saline-alkali soil the soil ESP and SAR got reduced, compared to the initial stage. Chen et al. [13] conducted one field experiment to know the performance of the alfalfa and soybean crops in FGD gypsum-applied sodic soil. From the experiment, they could find that the yield of the alfalfa and soybean got increased to 20-40 per cent and 5-10 per cent with the application of the FGD gypsum. The dry weight obtained from the alfalfa crops was higher when it was applied with FGD gypsum compared to control and gypsum-applied plots.

4. IMPROVEMENT OF SOIL PHYSICAL PROPERTIES

The use of FGD on land can enhance the physical qualities of the soil. Soils containing FGDs have less surface crusting and compaction, more water infiltration and holding capacity, higher aggregate stability, and less water runoff and erosion [16]. When FGD products are applied to the soil, the Ca^{2+} included in the products better flocculates soil particles (Fig. 3), improving soil attributes such as porosity, bulk density, water retention capacity, and accessible water content [17].

When the physical properties of the soil improve, it aids in the reduction of runoff and soil erosion. That is, any precipitation that falls on the soil will be absorbed straight into the soil layers rather than running off. The rate of soil erosion lowers as the rate of flow decreases [9]. Truman et al. [18] could arrive at a similar conclusion that when 9 Mg ha^{-1} amount of FGD gypsum was applied to the field the runoff rate could reduce by 40 per cent. Nan et al*.* [19] discovered that by applying FGD products to soil physical parameters such as bulk density, soil organic matter, soil total porosity, soil micro porosity, water retention capacity, and available water content, everything improved. Nevertheless, when humic acid and FGD products were administered jointly, they found that the effects were superior to the separate applications.

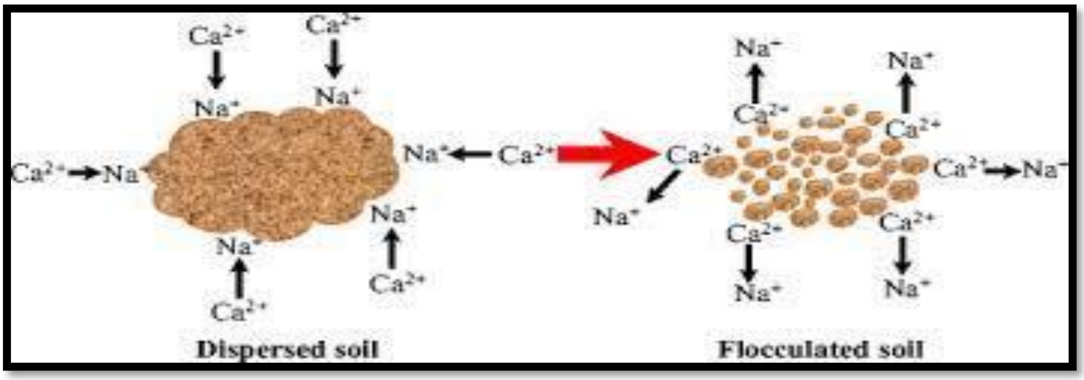

Fig. 3. Dissolved phosphorus with the application of the FGD products in the soil

5. SOURCE NUTRIENTS TO THE PLANTS

As FGD products are an excellent source of plant essential nutrients such as Ca^{2+}, Mg^{2+}, SO_4^{2-}, *etc.* applying them to the field improves the soil's nutritional status as well. But, before adding these FGD goods to the soil, we must first analyze the nutrient status, and then apply it depending on the soil's requirements. Because the boron and aluminium levels in FGD products are rather high, improper usage may result in nutritional poisoning [20].

6. REDUCTION OF PHOSPHORUS AVAILABILITY/TRANSPORT

Another advantage of using FGD on land is that it reduces the flow of P from high-P soils when substantial volumes of P-containing materials (e.g., chicken manure) have been put on land. Excessive amounts of P in surface soil can cause P loss in runoff water and consequent contamination of surface waterways. For example, outbreaks of the poisonous dinoflagellates alga *Pfiesteria piscidia* in streams have been linked to high levels of P in runoff water [21]. The use of FGDs with a high $CaSO_4$ concentration converts P in soil to less soluble forms, reducing runoff and P transfer to surface waters and potentially reducing P losses through leaching [22]. Excess P in runoff leads to water quality problems, including algal blooms and eutrophication of water bodies. FGD gypsum-filled trenches removed 50–95% of soluble P [23].

7. MISCELLANEOUS BENEFITS

FGDs combined with stabilising materials have been successfully employed to build pads that keep animals on firm surfaces and dry during the wet seasons of the year [24] turdy pads for storing and preserving dried hay for feeding animals throughout the winter season have also been built [24]. Combining FGDs with one or more additional by-products has been proven to be useful. FGDs and other CCPs have been effectively coupled with diverse organic materials (e.g., animal manures, biosolids, yard wastes, municipal solid wastes) for land and landscape application [25]. Several organic materials have been composted using FGDs with high alkalinity as sterilising and enriching agents. (e.g., biosolids, yard/wood/industrial wastes, manures) [26].

8. CAUTION ON THE USAGE OF FGD ON AGRICULTURAL LAND

1. Soil pH

Even at large application rates, FGD gypsum does not raise the pH of acidic soil. When alkalinizing compounds are included in the FGDs, soil pH rises. Even at moderate application rates, stabilised FGDs can significantly raise the pH of acidic soil, sometimes to unacceptably high levels [8].

2. Excessive soluble salts

Several soluble salts are often present in stabilised FGDs. If application rates are too high, they might be harmful to plants growing on soil altered with FGDs. This is especially true when too much B is used. Plants' sensitivity to soluble salts varies, and if excessive quantities are present, seed germination, plant establishment, and growth may be impaired. Plants classified as sensitive or moderately sensitive to salt may generally withstand EC values of 1.5 and 3.5 dS m-1 before adverse effects emerge (Maas 1990). Most FGDs do not have detrimental soluble salt effects unless large amounts are applied, and the danger of adding high levels of soluble salts is typically not an issue in the absence of nutritional imbalances and/or excessive B.

3. Boron toxicity

Boron is a soluble mineral component found in many of the materials added to FGD for stability, and B toxicity can be an issue for plants growing in soil modified with high B FGDs. Fly ashes often used to stabilize FGDs are high in B. While B is required by plants, the distinction between sufficiency and toxicity is narrow. Boron is also very soluble in water and easily leaches. B toxicity is often reduced once FGD-stabilized materials have been leached. Boron toxicity in field-grown plants may arise immediately after FGDs are applied to the soil, however, the toxicity was mitigated once rains leached B from the soil. (Clark et *al.,* 1999). Plants' vulnerability to B poisoning varies as well. In sensitive crops such as cherry, peach, and kidney beans, only modest doses of stabilized FGD should be used [9]. Alfalfa, as well as apple and pear trees, require very high amounts of B for optimal growth, but corn, cereal crops, and other trees are highly vulnerable to B poisoning. When fly ash-containing FGDs are applied to soil, the application rate must be adjusted to the crop's B requirement/sensitivity.

4. Excessive accumulation of nutrients in plants

To prevent plant buildup of high mineral element concentrations, FGD application rates must be controlled. Since FGDs contain high quantities of Ca and S, these elements may accumulate in excess in plants. Calcium may interact with a variety of mineral nutrients to cause mineral disorders/deficiencies or excess accumulation. Even though the FGDs had high amounts of Ca, young maize plants growing in acidic soil with non-stabilized and stabilised FGDs did not exhibit excessive leaf Ca concentrations (>10-15 g kg^{-1}) (Clark *et al.,* 1999). When plants were cultivated with equivalent doses of multiple FGDs, leaf S concentrations were near excess (>5.0 g kg^{-1}) (Clark et al., 1999). Plant S concentrations were higher in FGD-amended field soils than in un-amended plots for alfalfa and Bermuda grass, although S concentrations did not approach levels considered dangerous to animal ingestion (4.0–4.5 g kg^{-1}).

5. Heavy metal accumulation

The buildup of heavy metals in the soil is the main problem with the usage of these FGD products. The heavy metal content of FGD products, particularly non-stabilized and stabilized FGD, is greater. As a result, its improper application may result in the heavy metal deposition in the soil. Therefore, instead of using these goods, it is preferable to utilize FGD gypsum, which contains less heavy metal content. Chen *et al.,* 2001 did a field experiment and discovered that when FGD products with low levels of heavy metals are used for the experiment, the accumulation rate of heavy metals in soil and crop organs is lower, and we can use it safely in the agricultural field [27-29].

9. CONCLUSION

The FGD process is a new technique that is primarily used to remove the sulphur dioxide gas found in the flue gas released by thermal power plants. These FGD processes can minimise SO_4^{2-} emissions, hence reducing acid rain generation and environmental degradation. Non-stabilized FGD products stabilized FGD products, and FGD gypsum is the main product of these FGD processes. These waste products have a wide range of applications, including construction, cement preparation, and application in agricultural land. Almost 2% of total generation is used in agricultural land. Depending on the chemical nature of the FGD products, they can be used to improve acidic soil, soil sodicity, subsoil acidity, soil salinity, and so on. Before employing these goods in the agricultural field, we should properly check the chemical nature of the FGD products and apply them to the field based on the soil lime and gypsum requirements. Otherwise, it may lead to the opposite effect. It may be used to enhance soil physical qualities such as bulk density, soil organic matter content, soil porosity, soil water retention capacity, accessible water content, and so on, in addition to improving chemical status. The use of these FGD chemicals can help enhance the soil's nutritional condition. As a result, it is a beneficial resource rather than a waste product.

10. FUTURE LINE OF WORK

1. In India, an appropriate study on the application of these FGD products in agriculture was not conducted. As India has a significant number of thermal power plants, a considerable amount of FGD goods will be generated. If these generated FGDs are not used appropriately, they will become garbage and cause environmental issues. So, research must be conducted in order to turn these waste products into usable ones.
2. No studies have been undertaken to compare the performance of FGD gypsum to mined gypsum. So it must be done.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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