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FGD Gypsum- An Alternate Amendment for Sodic Soil

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ABSTRACT: Recently, there has been a surge in interest for using gypsum as a management technique to boost agricultural yields and improve soil and water quality. This interest has been fueled by the abundant quantity and availability of flue gas desulfurization (FGD) gypsum, a by-product of removing sulphur from combustion gases at coal-fired power plants, in key agricultural producing regions over the last two decades. Although it is typically cost-effective to employ FGDG as a soil amendment, its application in agriculture is extremely limited when compared to other industries. FGDG has several agricultural applications as a remediation material, including enhancing soil physicochemical qualities, limiting soil and nutrient loss, replenishing trace elements for soil, and increasing crop production. FGDG, on the other hand, contains a number of toxic trace elements. Long-term research of the influence of FGDG on soil health, heavy metal uptake, crop growth and quality, and ongoing monitoring of the health of soil and water should all be prioritized.

Keywords: Soil quality, water quality, gypsum, FGD gypsum, sulphur, soil properties

INTRODUCTION

Sulfur oxides (SOx) are released into the environment from two different sorts of sources: natural and anthropogenic. Geothermal, oceanic, vegetative, and terrestrial emissions are examples of natural sources. Natural sources account for 20% of total sulphur oxides released into the environment, while anthropogenic sources account for the remaining 80%. Sulfur emissions are caused by companies that use high-sulfur-content fossil fuels or industries that use sulfur-containing raw materials (e.g., sulfuric acid and ammonium sulphate manufacturing plants). Sulfur oxides are a primary source of anthropogenic emissions produced by the combustion of coal, crude oil and crude oil-based fuel oil, and gaseous fuels. In 1990, the United States, the Soviet Union, and China were the world's top sulphur dioxide emitters (accounting for over half of the total). Due to varied control techniques, the USSR and the US have stabilised their sulphur emissions during the last 20 years, and current increases in world sulphur emissions are tied to Asia. The pattern of fossil fuel consumption is shifting in response to a changing global context. At the moment, the world's primary energy production from coal and natural gas is estimated to be approximately 23.3 percent, while crude oil production is estimated to be around 38.5% (Panday *et al*., 2018).

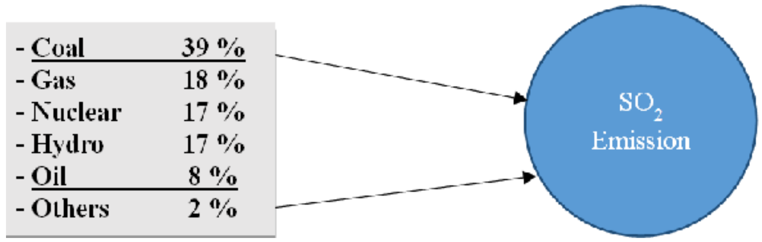


Fig. 1. The fossils fuels responsible for SO_2 emission.

Sulfur dioxide emissions are known to harm not just the environment, such as flora and animals, as well as historical sites like the Taj Mahal, but also human health. Breathing difficulties related with the upper respiratory system, irritation of the eyes, nose, and throat, and premature mortality are among the major health problems linked with high sulphur dioxide concentrations. Sulfur dioxide is converted to sulphur trioxide (SO_3), which is very soluble in water and resulting in sulfuric acid rain. By reducing the pH of water, acid depositions can harm freshwater lakes and stream ecosystems. This has an impact on species variety, fish numbers, and other aquatic flora and fauna. Buildings, stones, and ferrous and nonferrous metals can all be harmed by sulphur oxides. The reaction produced sulfuric acid. In India, regulations stipulate that the yearly arithmetic mean SO_2 content should not exceed 60 g/Nm^3 (normal cubic metre of gas at STP). The Indian Central Pollution Control Board (CPCB) has established three distinct criteria for SO_2 in the ambient air: 120 g/Nm^{3}for industrial regions, 80 g/Nm^3 for residential areas and 30 g/Nm^3 for sensitive areas, all based on a 24-hour yearly average. These areas' average annual concentrations should not exceed 80 g/Nm^3, 60 g/Nm^3, and 15 g/Nm^3, respectively. Precombustion, combustion or post combustion flue gas desulfurization processes must be used to meet regulatory criteria for SO_2 emissions into the atmosphere. The MoEF & CC criteria for coal-based thermal power plants comes into force in December 2015. The new regulations aim to dramatically reduce emissions of particulate matter (PM), sulphur dioxide (SO_2), mercury, and nitrogen oxides (NOx). SO_2 is one of the most dangerous pollutants emitted by thermal power plants. To satisfy new emission regulations announced by the government in 2015, a considerable number of India's coal-based thermal power stations will install flue gas desulphurization (FGD) systems by 2022. Most FGD systems used to regulate sulphur dioxide (SO_2) emissions use limestone as a main raw material. India is the world's largest SO_2 producer, accounting for more than 15% of worldwide anthropogenic emissions. Installation of FGD systems in power plants would be required to control these emissions. In India, only seven gigawatts of coal-fired power generation are fed by FGD systems. In the thermal power sector, there were no national regulatory guidelines for SO_2 emissions until 2015.In power plants, FGD systems are used to remove SO_2 from the flue gas. Flue gas is sprayed with a reagent (usually wet limestone) that combines with the SO_2 in the flue gas to produce calcium sulphate dihydrate [$CaSO_4 \bullet 2H_2O$], generally known as gypsum. The procedure restricts the amount of SO_2 released into the atmosphere. Limestone is a plentiful resource in India, with 200 billion tonnes of reserves. India's limestone output has been gradually increasing, and it now ranks among the world's top producers, with 338 million tonnes produced in 2017–18. According to CSE, operating FGD systems in coal-fired power plants would require only seven to ten million tonnes of limestone per year. This is less than three per cent of India's present limestone consumption. The quality of FGD gypsum is comparable to or better than that of mineral gypsum, and it has become a global substitute for mineral gypsum. China can use more than 70% of the FGD gypsum it produces. Because gypsum is a limited resource in India, adopting FGD would allow India's power plants to produce roughly 12–17 million tonnes of gypsum, which would supply domestic demand and lessen import burden. In 2014–15, India consumed roughly ten million tonnes of gypsum, of which it only produced 2.5 million tonnes and imported the rest.

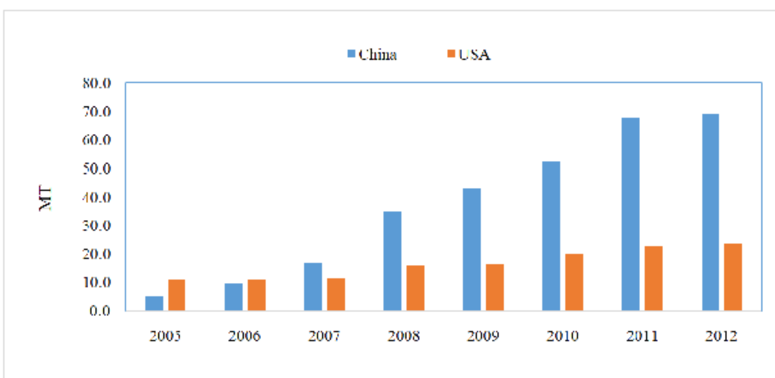


Fig. 2. Generation of FGD gypsum in China and USA (Source: Wang and Yang, 2018).

FGD (FLUE GAS DESULPHURIZATION) PROCESS AND MANUFACTURING

A. FGD Process

Method for removing SO_2 from released gas after combustion from fossil-fuel power plant exhaust flue gases.

(i) **Flue Gas Desulphurization Gypsum (FGDG).** The industrial by-product flue gas desulfurization gypsum (FGDG) is produced during the flue gas desulfurization process in coal-fired power plants.

(ii) **Manufacturing.** After coal combustion, flue gas desulfurization (FGD) gypsum is produced in limestone-forced oxidation scrubbers that remove sulphur dioxide from the flue gas stream. The flue gases are initially exposed to a slurry of hydrated lime in a wet scrubbing procedure. Calcium sulfite

($CaSO_3$•0.5H_2O) is formed when SO_2 is captured by the lime slurry. By introducing more air into the system, the calcium sulfite is oxidised and converted to gypsum ($CaSO4$•2H_2O).Washing the by-product can remove some water-soluble components like boron during and after the oxidation process (B). Fines removal can also lower mercury (Hg) readings in rare circumstances. A mixture of centrifugation and vacuum filtering is used to remove some of the water in the final step of the process.

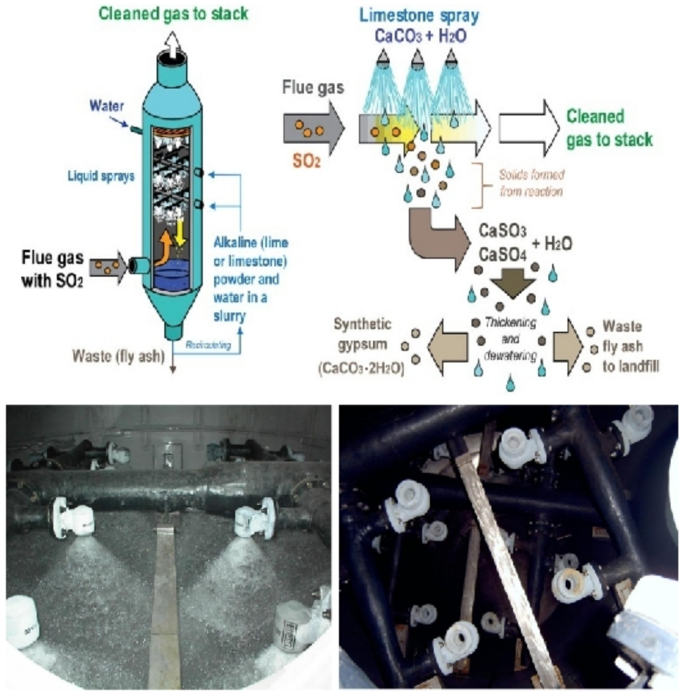


Fig. 3. FGD Gypsum production in thermal power plants.

The area where Limestone ($CaCO_3$) suspension is injected through Spray Header and Nozzle, SO_2 of combustion gas is absorbed

SALT AFFECTED SOILS AND THEIR EXTENT

Salt-affected soils are found across 954 million hectares (Mha) of land in 120 nations, and they contribute to a productivity loss of 7–8%. (Meena *et al.*, 2019). As indicated in Table 1, Australia has the largest area of salt-affected soils, accounting for more than half of all sodic soils worldwide (Shahid *et al.*, 2018). India currently has 121 million hectares of degraded land, with salt-affected soil covering 6.73 million hectares (NAAS, 2012). In India, there are 2.96 million hectares of saline soil and 3.77 million hectares of sodic soil (Tripathi, 2011). As a result, 2% of India's total geographic area is salt-affected, posing a threat to the country's long-term agriculture and food security.

Table 1: Salt affected soils and their extent.

Name of Country	Salt-affected area
Australia	30% (total area)
Thailand	30% (total area)
Egypt	9.1% (total area)
Hungry	10% (total area)
Iran	28% (total area)
Kenya	14.4% (total area)
Nigeria	20% (total area)
Russia	21% (total area)
Syria	40% (total area)
Tunisia	30% (total area)
USA	25-30% (total area)
India	4.2% (total area)
China	4.88% (total area)

(Source: Shahid *et al.*, 2018)

INDIA'S GYPSUM PRODUCTION

With annual imports of 3–5 million tonnes, India is one of the world's top gypsum importers. Oman, Pakistan, Iran, and Thailand are the largest suppliers of gypsum. Domestic mines, synthetic and marine gypsum, and domestic mines are the other significant sources for meeting demand. Rajasthan has 82 percent of the national gypsum deposit, while Jammu and Kashmir has 14 percent. The rest is split between Tamil Nadu, Gujarat, Himachal Pradesh, Karnataka, Uttarakhand, Andhra Pradesh, and Madhya Pradesh. 24 Rajasthan is the most important producer, accounting for nearly all of the entire output. Jammu and Kashmir contribute the remaining one percent.

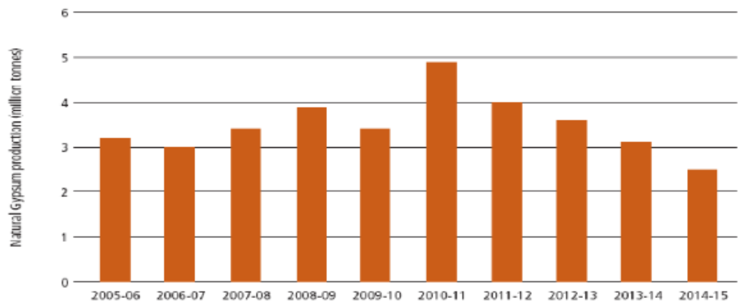


Fig. 4. India's gypsum production (Source: IBM, (2017).

ADVANTAGES OF FGD GYPSUM

FGD gypsum is increasingly replacing mineral gypsum due to its equivalent quality; as a result, gypsum supplements can improve the physical qualities of some soils (especially heavy clay soils). In the soil, such supplements provide a number of advantages.

Advantages:

- Help prevent dispersion of soil particles,
- Promote soil aggregation
- Reduce surface crust formation,
- Promote seedling emergence, and
- Increase water infiltration rates and movement through the soil profile.
- It can also reduce erosion losses of soils and nutrients and reduce concentrations of soluble phosphorus in surface water runoff.

COMPARISON BETWEEN FGD GYPSUM AND MINED GYPSUM

Gypsum comes in a variety of forms, each with its own set of mineralogical, physical, and chemical characteristics. The properties of FGD gypsum are frequently compared to results obtained from the same measurements for mined gypsum currently used in agriculture. Table 2 compares the mineralogical and physical parameters of FGD gypsum from Duke Energy's W. H. Zimmer Station (Moscow, Ohio) and mined gypsum from the Kwest Group (Port Clinton, Ohio). $CaSO_4{\bullet}2H_2O$ is the most common mineral found in FGD gypsum and mined gypsum. FGD gypsum occasionally contains trace amounts of quartz (SiO_2). Both quartz and dolomite [$CaMg(CO_3)_2$] are found in mined gypsum. Agriculturally mined gypsum that is granulated to generate a final size of 2–4 mm usually has a significantly smaller and more uniform particle size (more than 95 percent 150 microns). FGD gypsum, on the other hand, can be treated into bigger granules.

Table 2: Comparison between FGDG and Mined Gypsum.

Property	Unit	FGD Gypsum	Mined Gypsum
Minerals present		Gypsum, Quartz	Gypsum, Quartz, Dolomite
Water content	%	5.5	0.38
$CaSO_4.2H_2O$	%	99.6	87.1
Insoluble residues	%	0.4	13.0
Particle size			
>250 microns	%	0.14	100
Ca	%	24.3	24.5
S	%	18.5	16.1
Elements of Environmental concern			
As	(ppm)	< 11	462
Ba	(ppm)	5.5	76
Cd	(ppm)	< 1.0	< 0.12
Cr	(ppm)	< 1.1	10.4
Pb	(ppm)	< 5.0	100
Se	(ppm)	< 25	< 0.60

(Source: Dontsova *et al*., 2005)

HEAVY METALS CONCENTRATION IN FGD GYPSUM

Concentrations of heavy metals as used by different researchers in their studies was given below in Table 3. It is found that their concentration was below the standard (Permissible limits) fixed by the China government (Yang *et al.*, 2018).

Table 3: Concentration of Heavy metals in FGDG used in reclamation studies (Conc. in mg/kg).

References	As	Hg	Cd	Cr	Pb
Zhao *et al*. (2019)	2.71	0.17	0.49	21.31	14.86
Zhao *et al*. (2018)	7.4	9×10^{-1}	2×10^{-1}	43.6	1.3
Li *et al*. (2012)	5.1	0.2	ND	0.47	14.7
Koralegedara *et al*. (2019)	2.17	0.54	0.4	5.67	1.59
Standard	75	5	5	250	250

INFLUENCE OF FGD GYPSUM ON SOIL PROPERTIES AND CROP PRODUCTION

A. FGD Gypsum impact on soil erosion

Gypsum is the most commonly used amendment for sodic soil reclamation. The basis for this is that gypsum provides Ca that can exchange with Na and Mg, thus leading to flocculation of soil particles (Yonggan *et al.*, 2020). This promotes better overall structure development in these soils so that sufficient infiltration and percolation of water into and through the soil profile can take place (Liao *et al.*, 2019).

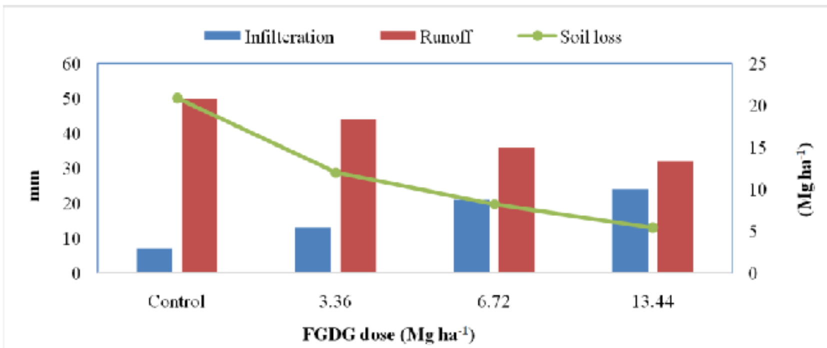


Fig. 5. The effects of FGD gypsum amounts on soil erosion parameters of the Bonn soil.(Source: Norton and Rhoton, 2007).

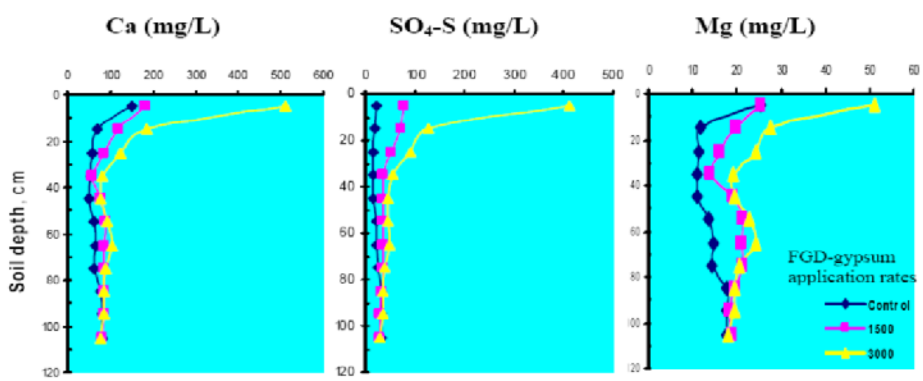


Fig. 6. Effects of surface applied FGD-Gypsum on water soluble Ca, SO_4-S and Mg at different depths. (Source: Chen *et al*., 2005).

B. Role of FGD gypsum on water soluble Ca, SO_4-S and Mg

Water soluble Ca and S were raised to a depth of 80 cm by FGD gypsum treatments (Fig 6). Even though the FGD-gypsum contained relatively low levels of total Mg, the amount of water soluble Mg increased. This finding, together with a drop in the soluble Ca/Mg ratios, suggested that soluble Ca from applied gypsum displaced Mg on the soil exchange complex.

C. Change in soil pH with FGD gypsum application

The pH of all soils was dramatically reduced by FGD-gypsum. FGD-gypsum has been proven in studies by Chun *et al*. (2001); Zhao *et al*. (2018) to slightly lower soil pH and maintain it for an extended duration in agricultural fields. This is because ExNa regulates the pH of soil colloids and water-soluble HCO_3 + CO_3^{2}. FGD-gypsum increased the amount of Ca^{2+} in the soil, which then reacted with HCO_3 + CO_3^{2-} to create $CaCO_3$ precipitation. Furthermore, Ca^{2+} might take the place of ExNa, which is leached down to the deeper soil layers. FGD-gypsum application caused these ions to rapidly drop, lowering soil pH.

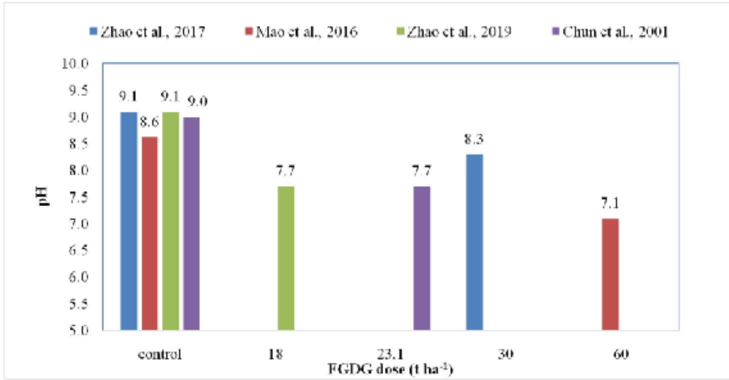
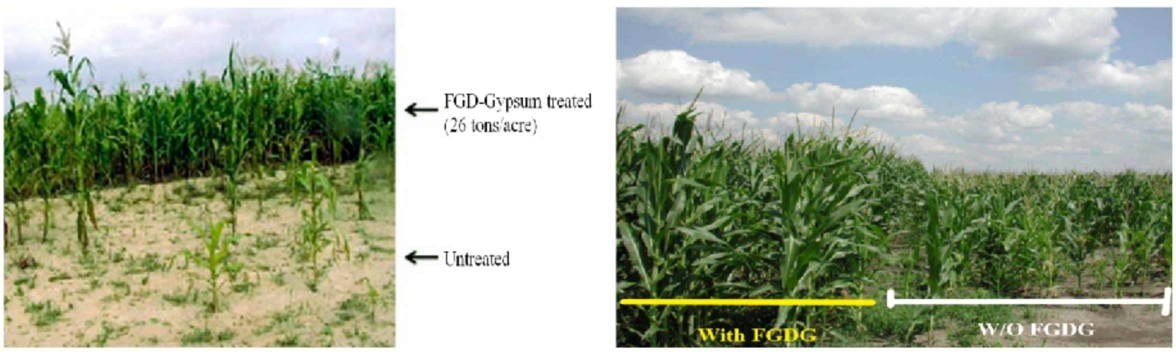


Fig. 7. Effects of applied FGD-Gypsum on soil pH.



(A) and (B) showing Maize crop growth with and without FGD gypsum application (Source: Xu, 2006).

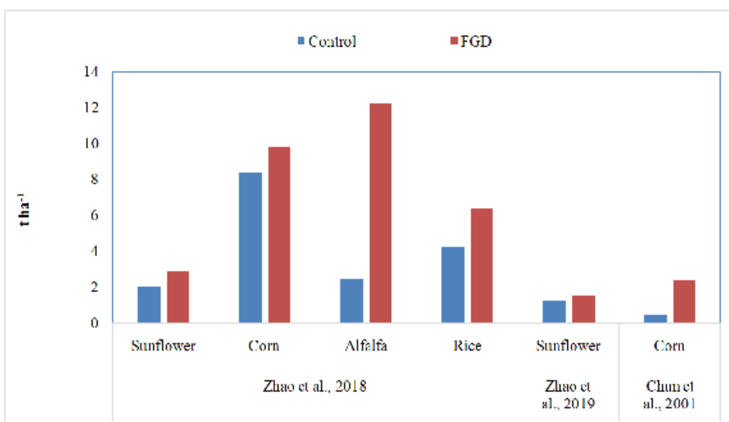


Fig. 8. Effects of applied FGD-Gypsum on crop yield (t ha^{-1}).

D. Influence of FGD gypsum on crop yield of different crops

Crop yields rose over time after reclamation using FGD gypsum. The continuous decreases in soil EC, pH, and ESP levels after reclamation with FGD gypsum can be linked to the steady increases in crop yields (Fig. 8). Furthermore, FGD gypsum application increased the soil organic content, physical characteristics and microbial community (Islam *et al.*, 2021). Furthermore, the FGD gypsum aided root growth by raising the concentrations of critical mineral nutrients (such as Ca, S, K, and B) while decreasing the availability of harmful components (Al, Mn, Cd, Cr, and Pb). However, because FGD gypsum is somewhat soluble in soil, it slowly releases calcium and sulphur with time.

E. Concentration of heavy metals in plants after FGD gypsum application

There were no significant differences in the metals content of crops between the study fields. In addition, all the metals content in crops grown in the reclaimed fields was far less than the national standards for food safety in China (GB 2762-2017), regardless of the variations in the levels between crops.

Table 4: Concentration of Heavy metals in plants (mg kg^{-1}).

Crops	As	Hg	Cd	Cr	Pb
Rice*	0.006	0.007	0.005	0.2	0.04
Sunflower seeds**	0.003	0.005	0.024	0.263	0.018
Corn seeds**	< 0.001	0.004	0.008	0.582	< 0.001
Alfalfa**	0.054	0.013	0.015	0.354	0.066
Rice**	0.003	0.005	0.004	0.126	0.004
Std GB2762-2017	0.2	0.02	0.2	1.0	0.2

*Zhao *et al*. (2019): **Zhao *et al*. (2018)

Heavy metals concentration present in seeds or grains of different crops plants as shown in the (Table 4) are found to be below the permissible limits (As, Hg, Cd, Cr and Pb). It is safe to human consumption as well as for livestock without deteriorating human – livestock health.

F. Concentration of heavy metals in reclaimed soil by FGD gypsum application

There were no significant variations in heavy metal (Cd, As, Pb, Hg, and Cr) content in the topsoil (0–20 cm) between the starting soils and the reclaimed soils after reclamation with FGD gypsum. When compared to the standard threshold of Std GB15618-2008 for soil, heavy metal concentrations (As, Hg, Cd, Cr, and Pb) were found to be within safe ranges (Table 5). As a result, there is no risk of heavy metal contamination in reclaimed soil when FGD gypsum is applied to the soil. The United States Environmental Protection Agency (US EPA) and the United States Department of Agriculture (USDA) authorised Agricultural Uses for FGD-gypsum in 2008, believing that its use in agriculture is safe under the right soil and hydrogeologic conditions.

Table 5: Concentration of Heavy metals in soil (mg kg^{-1}).

References	As	Hg	Cd	Cr	Pb
Reclaimed soil					
Zhao *et al*. (2018)	14.6	2 × 10-2	2 × 10-1	34.9	14.4
Zhao *et al*. (2019)	11.96	0.02	0.21	49.51	15.52
Std GB15618-2008	25	1.5	1	350	80

FGD SYSTEMS IN INDIA

In India, only seven gigawatts of coal-fired power generation are fed by FGD systems. In the thermal power sector, there were no national regulatory guidelines for SO_2 emissions until 2015. State-wide SO_2 emission standards were passed in some states, such as Gujarat, but they were not enforced. In December 2015, the Ministry of Environment and Climate Change (MOEF & CC) established new pollution standards for coal-fired power stations.

The plants were supposed to achieve the new standards by December 2017 according to the original notification. However, the Central Pollution Control Board (CPCB) has extended the deadlines for meeting SO_2 standards from 2017 to 22. According to the Central Electricity Authority's (CEA) FGD implementation plan, FGD installation is feasible in around 170 GW of total capacity out of 196 GW total capacity. Out of this, FGD has been planned for 161 GW of capacity.

Table 6: Source: FGD footprint in India.

FGD footprint in India	
Power Station	Capacity of the plant connected to FGD (MW)
Tata Trombay	750
Reliance Dahanu	500
Udupi TPP	1,200
Adani Mundra	1,980
JSW Ratnagiri	1,200
NTPC Vindhyachal stage V	500
CLP India	1,200
IL&FS Cuddalore	1,200
NTPC Bongaigaon	750

(Source: Centre for Science and Environment, 2019)

CONCLUSION

As more coal-fired power plants come online and current power plants add SO_2 scrubbers to meet with clean air regulations, annual FGDG production will skyrocket. The use of FGDG as a resource material in agriculture has long been recognised. Due to concerns about significant mental harm, such as the presence of toxic heavy metals in FGDG and leaching issues, it is necessary to incorporate FGDG into agriculture more effectively in order to fully exploit its various physical and chemical properties, which are beneficial to soil and crop health. Because it includes a significant number of important nutrients for plant growth, such as macronutrients like Ca, S, and Fe, Mg, and K, as well as micronutrients like Se, Mn, Zn, Cu, B, and Mo, FGDG's potential for usage in agriculture is gaining popularity. It is capable of reclaiming deteriorated soils. Applying FGDG to deteriorated soils can enhance physicochemical qualities, boost plant development, and improve crop quality. As a soil ameliorant, FGDG can reduce net CO_2 and SO_2 emissions, improving environmental quality and lowering global warming. Furthermore, using FGDG can help enhance water quality by reducing the migration of silt, minerals, and agricultural pollutants into surface water. FGDG appears to hold the most potential in terms of giving agricultural advantages with low environmental effect. Despite the benefits of utilising FGDG in agriculture, many people should be concerned about its heavy metal content, even though studies have shown that it is safe provided FGDG is administered in regular quantities and allows for heavy metal distribution through several release pathways (*i.e*., air emission, uptake in grass, and soil leachate). There are large regions of degraded soils around the world, particularly sodic soils, that could benefit from the use of FGDG.

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