Characterization and abatement of SO_x, NO_x and PCDD/Fs in iron ore sinter machine wind legs

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Abstract

It was observed that SO_x and NO_x, in large concentrations, are getting released from certain wind boxes below the sinter machine. The particulates released from specific wind legs were characterized using Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN). Particulates with spherical, cubical, needle and bar-like morphologies containing K, Na, Cl were found. Nitrogen-based solids were found in clutter-like morphology. Some particles had a mixture of the above, SO_x and NO_x. A method of dissolving SO_x, NO_x and breaking them down into harmless substances was explored in this research. The deposits in the wind legs were dissolved in demineralized water and solutions of sodium bicarbonate, urea, and di-sodium borate deca-hydrate (borax) to estimate the absorbance of K, Na, Cl, Ca, Mg, S, and N based compounds present. Demineralized water and sodium bicarbonate were found to be the most effective sorbents of SO_x and NO_x. The filtrates were examined under QEMSCAN and found that SO_x and NO_x are not present. Based on the above finding, a solution of sodium bicarbonate and water 0.01% v/v was sprayed into a wind box and found that SO_x and NO_x have got reduced by about 55%. To maximize the capture of SO_x and NO_x, the solution was optimized at 0.02% v/v. With this novel technique, capital intensive Desulphurization (De-SO_x) and Denitrification (De-NO_x) installation can be avoided. Additionally, an economical solution to the Polychlorinated dibenzo para-dioxins and polychlorinated dibenzofurans (PCDD/Fs) emission was explored in this research. Various physicochemical mechanisms of forming harmful substances are described in this paper.

1. Introduction

The raw materials used in the iron ore sintering process are iron ore fines (-10 mm size), fluxes such as limestone and dolomite, solid fuel such as coke fines and anthracite (-3.15 mm size), and calcined lime (-1 mm size). These materials are mixed thoroughly, granulated by spraying the water, and charged over the continuously moving sinter machine. The top layer of the sinter bed is ignited in the Ignition Furnace at about 1200 °C. As the atmospheric air is sucked through the sinter bed by the waste gas fan, the combustion zone gradually travels down into the bed, until it reaches the bottom. The iron ore particles are bonded together with the slag (containing silicates) formed by fusing limestone and dolomite. The solid fuel is the source of heat for the fusion process.

A sinter machine of 204 m² sintering area with 17 wind boxes and another sinter machine of 496 m² sintering area with 31 wind boxes were considered in this study. The temperatures of the gases in the 17 wind boxes, below the moving sinter machine, are continuously monitored for process control, as illustrated in Fig. 1. The direction of sinter machine travel is indicated with an arrow mark. The temperature of the gases in the wind box gradually increases from 100 °C to 120 °C due to preheating, up to wind box number 3, and then drops to about 70 °C due to the re-condensation phenomenon up to wind box number 10. It gradually starts to rise from wind box number 11–12 (153 to 240 °C, in Fig. 1) called *Burn-through Rise Point* (BRP) and reaches a maximum of about 400 °C called *Burn Through Temperature* (BTT). The point where BTT appears is called *Burn Through Point* (BTP): wind box number 15 in Fig. 1.

Iron ore sinter plants contribute to most of the emissions in Steel Plants (Fan et al. 2014; Han et al. 2014, 2019; Gan et al. 2016). It is important to understand the underlying reasons from the sustainability point of view and avoid closure. The conspicuous trail of smoke from the stack gives a bad impression of pollution in the onlooker's mind. This research work was taken up to reduce the emissions from the sinter plant stack.

The plume visibility is related to the concentration of SO_x, condensing into a mist; water vapor, and particulates (Kasama et al. 2009; Aries 2011). Iron ore, limestone, and dolomite contain chlorine, copper, zinc; heavy metals such as lead, mercury, zirconium, molybdenum, cadmium; apart from alkalis such as Na, K, F in traces (Wang and Zhang 2020). While the sintering process proceeds, their compounds are released through the wind boxes. Some of these particles, while traveling, stick to the structural members in the wind tract. Electrostatic Precipitator (ESP) installed before the stack of the sinter plants filters out the coarse dust particles containing iron ore, Ca, Mg, silicates, alkalis, chlorides, fluorides, carbonates, sulfates, and oxides of

a range of elements (Cavaliere and Perrone 2016; Ji et al. 2017b; Lv et al. 2018b). The finer particles that fail to settle down in ESP (particulates) exit into the atmosphere through the stack and pose an environmental issue. The stack emission contains particulates of SO_x, NO_x, KCl, VOCs, PCDDs, and PCDFs (commonly referred to as PCDD/Fs) which pose health-related hazards (KAWAGUCHI et al. 2002a, b; Yu et al. 2019). The emission profile of SO_x, NO_x, and VOCs in sinter pot apparatus was investigated by Juexiu Li (Li et al. 2019). The effect of fuel type on NO_x emission was indicated through the mathematical model by Wenjie Ni (Ni et al. 2019). The major source of NO_x was reported as coke breeze containing fuel N (Hu et al. 2017a). The particulates of 20-micron size can be trapped in the activated carbon, 10-micron size in membrane filters but PM_{2.5} may pass through most of the filters commercially available (Lv et al. 2018a). Therefore, the size and shape of these particulates are important in the sense that the spherical particulates may slip through and bar-like morphology may get easily struck (Lanzerstorfer and Steiner 2016). Hence in this research, characterization and morphological study were taken up.

The particulates released from the bottom of the sinter machine are by and large light in weight. Some of them are native, such as micro fines present in the coke, calcined lime, limestone, dolomite, and iron ore fines. Some of them are recycled through ESP dust.

Due to the drying and re-drying phenomenon (as illustrated in Fig. 2), the loose and light particles get disconnected from the sinter mix granules and travel along with the stream of gas. The products of the reactions travel from the combustion zone down into colder sinter mix layers. Some of them are condensed back and some escape through the voids (Kasai et al. 2001a; KAWAGUCHI et al. 2002a; Kasama et al. 2009). This phenomenon is observed until the colder sinter mix is present below the combustion zone. The chemical analysis of the deposit in the entire wind tract starting from under-grate, wind boxes, wind legs, wind main, ESP electrodes and its internal structural members, the inlet of the waste gas fan, impeller, and the exit duct is characteristic of the various physical or chemical phenomenon occurring in that particular location.

Worldwide, various systems such as high-temperature bag filters; de-sulphurization, and De-NO_x systems are being installed after the ESP, to capture the particulates. The latter technologies are cost-intensive and increase the complexity in terms of recycling the by-products from such systems, regeneration of activated carbon, and so on.

The emission of compounds of K, Na, Ca, Cl, N and S are being studied by researchers either by proactively inhibiting their formation or by trapping them before getting released into the atmosphere. A variety of De-SO_x and De-NO_x systems is devised and the issue of SO_x and NO_x is being addressed successfully (Cores et al. 2015). Wetfine system was indicatively preferred to Airfine (Smit et al. 2000) and Catalytic Oxidation (Boscolo et al. 2008a). Activated carbon has been found effective in trapping particulates up to PM₁₀. Particles below 10 microns were found escaping through its pores (Lv et al. 2018a). Scrubbers were found to be effective but treating the polluted water was increasing the complexity (Rotatori et al. 2006; Copeland and Kawatra 2011). However, the above technologies are cost-intensive (CPCB 2004). They require a *waste gas reconditioning tower* to lower the temperature and De-SO_x, De-NO_x chambers that contribute to the cost. In our research on the recycling of sinter waste gas into the sinter bed, a reduction in particulate emissions was noticed (Angalakuditi et al. 2021). Selective Catalytic Reduction of NO_x is one of the successful methods, wherein 95% reduction is reported with the help of NH₃ gas and vanadium and tungsten catalysts. NO_x emission profile was investigated by Chin-lu Mo and Kenji Tiara (Mo 1997; Taira 2019, 2020). It was identified that the *NO_x conversion factor* in the combustion zone was related to the amount of NO_x released.

Calcium hypochlorite was tried, to dissolve SO₂ and NO_x, and about 85 to 100% removal was reported (Zhou et al. 2015b). They discussed chemical – thermodynamic aspects of dissolution and reactions. However, an engineered solution is much needed in commercial-scale sinter plants. Slack lime, gypsum, and sodium sulfate are the other recommended sorbents of SO_x and NO_x. Hydrated lime was coated on the coke fines used for making sinter and a drop in NO_x emission was reported by Katayama (Katayama et al. 2015). Ammonium sulfate was tried as an inhibitor of dioxins (Łechtańska and Wielgoński 2014). Inhibition of the formation of harmful compounds was effective by adding urea along with the raw materials (Aries

2011). Adding anthracite coal was reported to reduce SO_x, NO_x emissions. Due to the absence of aliphatic compounds in anthracite coal, harmful VOCs are not formed. Bio-fuels are tried by various researchers to suppress the formation of harmful substances (Gan et al. 2014; Fan et al. 2015). Charcoal was also administered in-lieu of coke fines (Lovel et al. 2007; Ooi et al. 2011; Lu et al. 2015; Cheng et al. 2016; Fan et al. 2016). Biomass and biogas were suggested by Jose Adilson de Castro (De Castro et al. 2013; de Castro et al. 2018) through mathematical models, as an alternative to reduce harmful emissions. Consumption of solid fuel has been substituted by the injection of LNG and Oxygen into the sinter bed and the CO₂, particulate emissions have come down (Oyama et al. 2011). In our research work, injecting hydrogen-rich gas into the sinter bed was tried to reduce the solid fuel consumption and thereby reduce the emissions (Acharyulu et al. 2021).

Evacuation of ESP dust and abstinence from direct recycling was found to be effective in JSW Steel, Vijayanagar Works. Use of up to 40% anthracite coal containing 2.5–2.75% volatile matter, as alternate solid fuel was being practiced and lower emissions are observed since the year 2011. About 3400 Nm³ of waste gas per ton of sinter is released into the atmosphere at a temperature of about 140 °C (or 1,100,000 Nm³/hr per machine of 2.5 MTPA capacity). The De-SO_x and De-NO_x systems installed before the stack, around the world do handle waste gas of this magnitude and hence are large in size and capital intensive. Handling the by-products of such systems increases the complexity further. JSW Steel, Vijayanagar Works produces about 13 million metric tons of iron ore sinter per annum and the volume of waste gas to be handled is very high (to the tune of 44,200 million Nm³ in a year).

The maximum SO_x and NO_x are in the concentration range of 380 and 350 ppm; while the concentration in the stack was in the range of 50 to 170 ppm. The velocity of the gas in these wind legs was in the range of 100 m/s and a flow rate of 300,000 Nm³/hr (83 Nm³/s) was observed. This flow rate is much smaller compared to the flow through the stack of 1,100,000 Nm³/hr (305 Nm³/s). The volume of waste gas per wind leg varied from 75 to 300 Nm³ per ton of sinter, depending upon its location from the feed end to the discharge end of the sinter machine. The typical velocity of the waste gas was in the tune of 60 to 100 m/sec; while the velocity in the stack was about 16 to 20 m/sec. It will be easier to handle the smaller quantity of waste gas and efficiently while the particulate concentration is high. It has been envisaged in this study to dissolve and break down the particulates in the wind boxes by spraying the solution of a variety of sorbents.

In this research, an attempt has also been made to provide a simple and cost-effective solution to abate the generic SO_x and NO_x in sinter machine wind legs. Various specific compounds such as SO₂, SO₃, NO, N₂O, and NO₂ separately were considered beyond the scope of work.

Additionally, an attempt has been made to address the generic PCDD/Fs issue. There are several compounds in the family of PCDD/Fs, the study of which was considered as beyond the scope of this work. PCDD/Fs are formed at a temperature above 1200 °C in the combustion zone of the sinter bed and are released when the reducing conditions are changed to oxidizing conditions (Salgueiro et al. 2003, 2004; Kasama et al. 2006a). A deposit in the ESP was spotted containing KCl and PCDD/Fs (Fig. 3). It was very light, looked like fleece, and has a density of 0.45 g/cm³. It has been dissolved in acetone, hexane, and toluene successfully. The PCDD/Fs are released from wind boxes 14, 15, and 16 where the gas temperature is in the range of 400–450 °C. The autoignition temperatures of acetone (C₃H₆O), hexane (C₆H₁₄), and toluene (C₆H₅CH₃) are 465, 223, and 480 °C respectively. Spraying these organic substances may not be safe in such a hot zone. A method to suppress the formation of PCDD/Fs by injecting inert gas such as nitrogen has been discussed.

2. Materials And Methods

The materials used in this research were deposits in wind legs, ESP hoppers and the electrostatic fields of the iron ore sinter plant of JSW Steel, Vijayanagar Works. Demineralized water, sodium bicarbonate, urea, and borax were used in the dissolution study of the particulates containing SO_x, NO_x. Acetone, Hexane and Toluene were used to see the dissolution of the deposit over the ESP fields containing PCDD/Fs.

Pulse-jet metering pump of Milton Roy make was used to spray the sodium bicarbonate solution into the wind legs. Sympatec GmbH make RODOS Micron Size Particle Analyzer was used for the size distribution of ESP dust particles. Wet chemical analytical method and Thermo Fisher make X-Ray Fluorescence Analyzer (XRF model 101/367) *Optiquant* method was used for assessing the contents of the ESP dust and wind leg deposits. FeO was evaluated by the wet chemical analytical method. LECO make Carbon Sulphur Analyzer SC832HT was used to find out the carbon and sulfur present in the wind leg deposits. Bruker make QEMSCAN (Quanta 650 FEG) was used to map the contents of the deposits in the wind legs and ESP 4A, 4B fields. The filtrates after dissolution were mapped using QEMSCAN and EDAX make TEAM Energy Dispersive Spectroscope EDS XFlash Detector 5030. Various APHA standards, IS-3025 series for assessing water quality were adopted to measure the dissolution of SO_x, NO_x, and chlorides. IMR make portable flue gas analyzer IMR-2800P was used to measure CO, CO₂, O₂, SO_x, NO_x and Horiba make Portable Gas Analyzer PG300 were used to measure SO_x, NO_x levels in the wind legs, following US EPA air quality monitoring guidelines and IS-11255. The assessment of PCDD/Fs was done according to USEPA Method 23A @ 11% oxygen.

3. Results And Discussion

The opacity at the exit of the Process ESP is a metric of visible emissions. The data of an industrial-scale sinter plant, for the last two years, was statistically analyzed to understand the effect of process parameters on opacity. The dependency of opacity (mg/Nm³) on calcined lime, VM in solid fuel, and Loss on Ignition (LOI) of iron ore fines are depicted in Fig. 4. To minimize the emissions, it is recommended to minimize the VM in the solid fuel, the micro fines in the raw materials, LOI in the iron ore fines, and usage of calcined lime (Zhang et al. 2015).

During the combustion of solid carbonaceous fuel such as coke breeze containing fuel N, S, P, and volatile matter, in the presence of other raw materials of the iron ore sintering process, harmful compounds are unintentionally produced. SO_x and NO_x are the most commonly experienced particulate emissions. Oxidation of organic sulfur, volatile matter (VM), and fuel N contribute to the formation of SO_x and NO_x. Typical content of sulfur, nitrogen, and VM in coke fines varieties A, B, C, D, and anthracite A, B, C are measured and given in Table 1. To control the SO_x, NO_x emissions, it is recommended to use solid fuel varieties containing lower sulfur and nitrogen.

Table 1
Nitrogen and Sulfur in solid fuel

Source of Solid Fuel	S, %	N, %	VM, %
Coke A	0.90	1.30	6.5
Coke B	0.38	1.10	4.6
Coke C	0.65	0.90	4.1
Coke D	0.47	0.80	0.76
Anthracite A	0.21	0.57	2.5
Anthracite B	0.32	0.64	2.9
Anthracite C	0.77	0.84	3.5

Low-temperature pyrolysis (in the shortage of air) is a source of SO_x, NO_x emissions in the iron ore sintering process (Yang et al. 2005; Zhang et al. 2015; Zhou et al. 2015a; Liu et al. 2020). Combustion of solid fuel (in the abundance of air) is the source of CO₂ and high-temperature emissions such as KCl and PCDD/Fs (Ji et al. 2017b; Yu et al. 2019). The melting point of KCl is 771 °C and the boiling point 1437 °C. The formation of KCl is exothermic as given in Eq. 1.

Nitrogen could be easily released in pyrolysis (Hu et al. 2017b). The organic substances liberated from the pyrolysis (tar as an example) join the gas stream, causing these particulates to stick to the structural members in the gas tract. As the particulates continue to impinge on the structural members, accretion, diffusion, and crystallization occur. Vapors of organic sulfur and phosphorous are formed at 280 and 444 °C respectively. The possible product compounds are SO₂, SO₃, SO₄, P₂O₅ depending upon the thermodynamic conditions. Fuel nitrogen, volatile matter, and other organic substances (regarded as *Loss on Ignition*) are also subjected to pyrolysis. The sticky deposits are observed in the wind legs 5 to 10 only. Beyond these wind legs, the sinter mix below the combustion zone gets sufficiently hot and the condensation of organic substances is forgone.

SO_x and NO_x content in the wind legs was measured with the help of IMR Gas Analyzer. The variation of SO_x and NO_x in wind legs is illustrated in Fig. 5 (a) for a sinter machine containing 17 wind legs and in Fig. 5 (b) for a sinter machine with 31 wind legs respectively. The sinter machine with 17 wind legs was of particular interest in this research work. The SO_x increased gradually to a maximum at wind leg 6 and then reduced beyond wind leg 10. NO_x gradually increased until wind leg 7, reduced at wind leg 8, and then increased to a maximum in wind leg 10. It persisted up to wind leg 13. It was noticed that corrosion was significant in wind legs 5 to 10. However, the distribution of SO_x, NO_x over wind legs varied from sinter machine to Machine and the variations in the sintering process. The trend of SO_x has got shifted to the farther wind legs 20 to 29 in sinter machine with 31 wind boxes and that of NO_x was seen between wind legs 4 and 25.

The CO₂ and O₂ content in the waste gas in the wind legs was measured with the help of IMR Gas Analyzer and is graphically represented in Fig. 5 (c) and (d). As the sintering process proceeds, due to the combustion of solid fuel, CO and CO₂ are released and the O₂ content gradually drops. After the combustion process is ended in the later stages of the process, O₂ content increases. In other words, reducing conditions change to oxidizing conditions after the BTP. Until then, the partial pressure of oxygen is low due to the prevailing reducing conditions. This phenomenon is very important in the formation of PCDD/Fs (Ooi and Lu 2011).

The sulfur, phosphorous, and nitrogen-based compounds react in the subsequent stages to form Na₂SO₄, CaSO₄, NaNO₃, Ca(NO₃)₂. At temperatures < 800 °C, some of the solid-state transformations such as CaO.Fe₂O₃, CaO.2SiO₂, CaO.2Al₂O₃ are completed and the resultant compounds are assimilated into the slag phase. The loosely held particles are released into the gas stream through voids (Yu et al. 2016). Silicates and carbonates combine with alkalis to form alkali silicates (Na₂SiO₃ and K₂SiO₃) and alkali carbonates (Na₂CO₃, K₂CO₃). Reaction with CO gas can also form K₂CO₃. The oxidation of alkalis Na and K takes place between 300 and 800 °C respectively and their vapors such as Na₂O and K₂O are released. The other stoichiometric compounds are NaO₂, Na₂O₂, K₂O₂, KO₂, and K₂SO₄ (Ji et al. 2017a). With the presence of chlorine, NaCl and KCl are formed (Ji et al. 2017b). They vaporize at high temperatures (1074 and 1400 °C respectively) and hence are released from the last wind boxes of the sinter machine (Kasama et al. 2006b; Ji et al. 2017a).

H₂S, H₂SO₄, and HCl are some of the acids formed owing to the hydrogen present in the fuel gas used for ignition and through the usage of water for granulation. Through water vapors, volatiles, and hydrated phases present in iron ore, hydrogen is available to form these acids. The CO and CO₂ gases are the other sources of reactions with SO₂. These acids are the major source of corrosion of wind legs and ESP collecting electrodes. Mist of acids and SO₃ also add to the visibility of the plume (Kasama et al. 2009; Aries 2011).

The chemical analysis of the deposit in wind leg 10 was assessed as given in Table 2, as an example. Some substances such as Fe₂O₃, SiO₂, Al₂O₃, MnO, TiO₂, and Cl are typically from raw materials. MgO is due to the calcination of dolomite. CaO is from calcined lime and calcination of limestone. Carbon is from carbonates and solid fuel. The other compounds SO₃, P₂O₅, Na₂O, and K₂O are from various reactions.

Table 2
Chemical analysis of the deposit in
wind leg 10

Substance	Content, %	
SiO ₂	3.190	2.950
Al ₂ O ₃	1.960	2.070
Fe ₂ O ₃	23.770	24.210
CaO	5.320	5.580
MgO	0.650	1.120
MnO	0.220	0.081
TiO ₂	0.113	0.088
P ₂ O ₅	0.106	0.570
SO ₃	17.210	5.690
Na ₂ O	0.227	0.390
K ₂ O	2.700	2.440
Cl	10.320	4.110
C	13.960	24.060
LOI	33.800	49.440

The release of PCDD/Fs varies as the sintering progresses (Kasama et al. 2006b; Qian et al. 2018). The first release of Furans in the tune of 20 ng/Nm³ was reported in the first wind leg, there were none until BRP. Similarly, dioxins were not noticed until BRP. Dioxins and Furans are released to the maximum in the tune of 100 and 60 ng/Nm³ at BTP. Release of PCCDs in the range of 180 and PCDFs up to 240 ng/Nm³ has been found followed by KCl, near Burn Through Point (BTP: the point where the temperature of the gas is maximum) in the sinter machine (Kasama et al. 2006b). They suggested that the gas temperature is critical to the release of PCDD/Fs and hence BTT has to be optimized to control the PCDD/Fs emissions. However, observing the O₂ content in the waste gas in the wind legs, it is evident that PCDD/Fs release is a function of oxygen content. Furans formation was noticed when oxygen was in the tune of 16% under the ignition furnace, where the temperature was in the tune of 100 °C only. Further, PCDD/Fs were not present until the O₂ was less than 10%. As the oxygen content increased near BTP, PCDD/Fs maximized.

In a thermodynamic model, Zhang (Zhang) indicated a terminal temperature of 1433 °C in the sinter bed. This is close to the boiling temperature of KCl, 1437 °C. At the end of the sinter machine, after *Burn Through*, since there is no sinter mix present, the high-temperature product particulates such as KCl, NaCl, and PCDD/Fs are released into the gas stream. The formation of PCDD/Fs is predominant as the partial pressure of oxygen increases i.e. more oxygen atoms are available to join chlorine atoms at a temperature above 1200 °C. The temperature of the combustion zone, as it touches the pallet car bottom was measured with the help of pyrometers and was in the tune of 1180–1220 °C. Hence an average of 1200°C was considered. The vapors of KCl, NaCl, PCDD/Fs re-condense in the top of ESP, near the exit where the velocity and temperature drop to a minimum and stick there.

Apart from the above Benzo (a) Pyrene (BaP), Volatile Organic Compounds (VOC), Poly Aromatic Hydrocarbons (PAH), PCDD/Fs are also released. Data of various compounds measured in the stack of JSW sinter plants are given in Table 3.

NO_x was considered as a major area to be focussed on. PCDD/Fs were in the range of 0.0014 to 0.0021 ng ITEQ/Nm³.

Table 3
Chemical analysis of sinter plant stack emissions

Substance	Protocol	Range, mg/Nm ³
Sulfur Dioxide (SO ₂)	IS:11255 (Part-2)	16 to 29
Nitrogen Oxide (NO _x)	USEPA 7E	215 to 318
Hydrogen Sulphide (H ₂ S)	IS:5182 (Part-7)	26 to 54
Ammonia (NH ₃)	USEPA 6A	12 to 23
Fluoride (F)	USEPA 26	2 to 5
Hydrochloric Acid (HCl)	USEPA 26	2 to 6
Mercury (Hg)	USEPA 29	0.1 to 0.7
Benzo (a) Pyrene (BaP)	CARB 429	0.02 to 0.07
Volatile Organic Compounds (VOC)	USEPA 31	2 to 4
Poly Aromatic Hydrocarbons (PAH)	EPA 429	0.02 to 0.07

Volatile Organic Compounds (VOCs) such as Polychlorinated Di-benzo Dioxins / Furans (PCDD/Fs) is another such area where commercially viable technology to suppress their formation is not developed so far. PCDD/Fs are isomers; have chlorine and oxygen atoms chained as shown in Fig. 6. According to the WHO report on Air Quality Guidelines, Chap. 5.5, PCDD/Fs are formed during combustion of carbonaceous substances, incineration of wastes, sludge especially chlorine-laden substances (Lebsanft and Basler 1992).

The family of dioxins and furans is shown in Table 4. On the toxicity scale, TCDD (Tetra Chloro Di-benzo p-Dioxin) is set as one (lethal), other variants are expressed as a ratio to TCDD or Toxicity Equivalent (TEQ). Sampling and analysis of PCDD/Fs are cumbersome (Environment 2003; Roudier et al. 2010; STA 2018), making the monitoring and controlling difficult. ESP dust was reported to contain 24 to 46 ng/g of Furans and 28 to 52 ng/g of Dioxins in two sinter plants (KASAI and AONO 2001; Kasama et al. 2006b). Recirculation of ESP dust along with the raw materials has indicated aggression in the formation of PCDDs (Boscolo et al. 2008b). Mixing rice husk and sugar into sinter mix reduced NO_x emission. (Mo et al. 1997). The deliberate addition of PVC and NaCl into the sinter mix has resulted in increased emission of PCDD/Fs, ascertaining that chlorine is the major source of PCDD/Fs formation (Kasai et al. 2001b). Hence sources of chlorine are to be regulated in the inputs. The absorbance of PCDDs in acetone, hexane, and toluene was indicated by Wan Ying Shiu (Shiu et al. 1988a).

Table 4
Family of dioxins and furans

Number of chlorine atoms	Dioxins	Number of isomers	Furans	Number of isomers
1	Monochloro dibenzo para-dioxin	2	Monochloro dibenzofuran	4
2	Dichloro dibenzo para-dioxin	10	Dichloro dibenzofuran	16
3	Trichloro dibenzo para-dioxin	14	Trichloro dibenzofuran	28
4	Tetrachloro dibenzo para-dioxin	22	Tetrachloro dibenzofuran	38
5	Pentachloro dibenzo para-dioxin	14	Pentachloro dibenzofuran	28
6	Hexachloro dibenzo para-dioxin	10	Hexachloro dibenzofuran	16
7	Heptachloro dibenzo para-dioxin	2	Hepta-chloro dibenzofuran	4
8	Octachloro dibenzo para-dioxin	1	Octa-chloro dibenzofuran	1
Total PCDDs		75	Total PCDFs	135

At the BTP, the sintering process is completed and the cooling effect of the sinter is evidenced in the remaining two wind boxes. The voidage increases soon after the sintering is completed and a huge amount of atmospheric air gushes through the last wind boxes. Therefore, it becomes difficult to arrest the formation of PCDD/Fs. Their formation can be minimized essentially by restricting access to oxygen.

3.1. Characterization of Particulates

The assessment of characteristics of the dust collected in the ESP is an important step in designing the ESP for maximizing collection efficiency (Lanzerstorfer and Steiner 2016; Lanzerstorfer 2017). The other critical properties of the dust are basicity (varies from 1.3 to 2.0), specific resistivity (3×10^{11} to $2 \times 10^{12} \Omega \text{ cm}$), and bulk density (0.68 to 1.2 g/cm^3). As the basicity and resistivity increase, the collection efficiency reduces (Khosa et al. 2003).

In the present study, samples were collected from each hopper of ESP 1A, 1B, 2A, 2B, 3A, 3B, 4A, 4B; wind legs no. 6, 7, 8, 9, 10 and ESP top chamber deposit near 4A, 4B fields. The dust samples collected from ESP hoppers were analyzed for size distribution and chemistry. The size analysis indicated that the particle size decreased from the inlet to the exit hopper of ESP; the finest particles being found towards the exit, as illustrated in Fig. 7.

The chemical analysis of the dust in the hoppers 1A, 1B, 2A, 2B, 3A, 3B, 4A, and 4B is given in Table 5. The dust contained relict particles from raw materials and the products of various reactions and condensates.

Table 5
Chemical analysis of the dust in the ESP hoppers

Hopper No.	1-A	1-B	2-A	2-B	3-A	3-B	4-A	4-B
Fe(T), %	44.550	39.400	40.460	41.270	40.730	40.290	41.970	40.610
FeO, %	3.310	2.870	2.850	2.800	2.880	3.020	3.170	2.880
SiO ₂ , %	8.120	7.250	8.140	8.030	8.170	7.310	7.640	7.850
Al ₂ O ₃ , %	4.320	4.000	4.300	4.320	4.470	4.020	4.140	4.220
CaO, %	10.870	12.490	11.730	11.300	12.260	12.030	11.700	11.300
MgO, %	2.580	2.340	2.700	2.590	2.730	2.380	2.440	2.500
MnO, %	0.277	0.263	0.263	0.260	0.268	0.265	0.273	0.258
TiO ₂ , %	0.181	0.168	0.172	0.167	0.177	0.168	0.171	0.166
P, %	0.051	0.050	0.049	0.051	0.048	0.044	0.048	0.049
S, %	0.700	1.240	0.990	0.750	1.080	1.120	1.140	1.190
Na ₂ O, %	0.141	0.457	0.309	0.371	0.309	0.477	0.300	0.370
K ₂ O, %	0.560	2.140	1.100	1.240	1.110	1.590	1.100	1.270
ZnO, %	0.010	0.011	0.011	0.010	0.010	0.012	0.011	0.009
Cl, %	1.210	2.880	2.000	2.130	2.060	2.780	2.010	2.280
Cr ₂ O ₃ , %	0.040	0.036	0.046	0.039	0.025	0.029	0.031	0.034
PbO, %	-	0.037	0.022	0.025	0.020	0.031	0.021	0.026
V ₂ O ₅ , %	0.017	0.009	0.010	0.009	0.011	0.013	0.009	0.011
C, %	4.000	4.720	4.210	4.370	4.400	4.780	4.400	4.600
LOI, %	7.660	10.700	10.710	10.080	9.400	10.530	9.370	10.900
Basicity	1.340	1.720	1.440	1.410	1.500	1.650	1.530	1.440

The samples of deposits in wind legs and ESP fields 4A, 4B were exclusively studied with the help of QEMSCAN for morphology and elemental analysis. After characterization, they were dissolved in various solutions to see how much S, N, and Cl compounds got dissolved, specifically. The filtrates left out thereby were again examined under QEMSCAN to ascertain that the above compounds were not present.

The samples of the deposits on the wind legs were assessed for the presence of Carbon and Sulphur in the Coal Characterization Laboratory using Carbon – Sulfur Analyzer. The result is shown in Table 6. The content of sulfur followed the pattern of SO_x formation, along the length of the sinter machine. The carbon content increased initially, decreased later, and then shot up sporadically. After wind leg no. 10, no deposits were found; indicating that the unburnt fine solid fuel particles or carbonates were released in the drying section of the sinter bed in two phases.

Table 6
Carbon Sulfur Analysis of the deposits in
wind legs

Wind Leg No.	Carbon, %	Sulfur, %
6	14.70	2.03
7	15.80	3.74
8	10.00	4.94
9	4.44	5.82
10	14.60	7.45

The presence of carbon and sulfur in large quantities is related to the drying phenomenon occurring in the sinter bed, above these wind legs. The first phase corresponds to the primary drying, where the moisture in the green mix gets released due to the combustion of solid fuel. As the vapor travels down into the colder bed, it gets re-condensed, increasing the moisture. As the combustion zone travels further down, this layer also gets dried by releasing the excess moisture. At this point, another batch of fine solid fuel or carbonate particles is released (secondary phase, Fig. 2). It is also intriguing to note that most of the low-temperature particulates are released well before Burn-through Rise Point (BRP).

The chemical analysis (in %) of the deposits in the wind legs is given in Table 7.

Table 7
Chemical analysis of the deposits in wind legs (in %)

Wind Leg No.	6	7	8	9	10
Fe ₂ O ₃ , %	28.3600	35.7600	40.6200	26.8800	21.7800
CaO, %	6.0500	9.8000	8.4100	8.4200	7.9100
SO ₃ , %	4.4400	5.8500	5.0700	16.5700	6.1500
SiO ₂ , %	1.6600	2.5100	2.6000	1.7400	1.6300
Al ₂ O ₃ , %	0.6260	0.8990	0.8090	0.7200	0.6600
K ₂ O, %	0.9580	0.0757	0.1370	9.6800	0.5270
Cl, %	0.0378	0.3200	0.1650	0.0400	0.0711
MgO, %	0.5160	0.5780	0.5360	0.7330	0.3080
MnO, %	0.1840	0.2040	0.2500	0.2820	0.1810
Na ₂ O, %	1.0700	0.1300	0.2140	3.2200	0.0000
S, %	1.7800	2.3400	2.0300	6.6300	2.4600
P, %	0.0819	0.1070	0.1040	0.0304	0.0785
TiO ₂ , %	0.0742	0.1070	0.0972	0.0827	0.0657
ZnO, %	0.0039	0.0191	0.0147	0.0293	0.0136
LOI, %	55.9600	43.5600	40.9300	31.1500	60.5700
Basicity	3.6446	3.9044	3.2346	4.8391	4.8528

3.2. Morphological Study using QEMSCAN

The deposits in the wind legs 6 to 10 had a variety of morphology as seen with QEMSCAN. The scanning specifications were: 20 kV; K α Series for N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, and Zn; L α series for Zr, Mo, Cd, Pb. Compounds containing Ca, Si, Al, Na, K, S, and N are found in varying morphology and size, as shown in Fig. 8 to Fig. 16. In this section, the scanned images are given followed by the spectrum and a table of elemental analysis. The bar/rod/cube/sphere/plate-like morphologies observed are due to crystallization. The sticking of particulates to each other is due to diffusion, as noticed in Fig. 15. The non-crystalline substances are seen as clutter (without a prominent shape) in Fig. 8 and Fig. 14 (E).

The deposition on its inspection door revealed the mechanism of deposition. The needle-like particles were found to impinge continuously, assimilate and appear star-like particles. Wei LV et al (Lv et al. 2018a) had reported similar micrographs.

Chlorine was seen as globules: K & Cl were found on ball-like particles. Impingement of various particles on substrate indicated signs of inter-particle diffusion and assimilation (Ji et al. 2017b; Lv et al. 2018a). Hence bar-like particles appeared as stars in Fig. 15.

3.3. The Concept of Dissolving as a Means of Abatement

In the commercially available technologies, the harmful substances such as SO $_x$, NO $_x$ are either dissolved in water spray (scrubbers), reacted with ammonia, urea (Aries 2011; Chun et al. 2017) or passed over catalysts or trapped in the pores of the activated carbon (Han et al. 2014; Lv et al. 2018a). It was understood that wet scrubbing was one of the most effective methods of capture (Copeland and Kawatra 2011). In this technique, the water dissolves and carries away sulfur and nitrogen compounds. The concentration of sulfur and nitrogen in the water increases after dissolution. This technique was adopted in this research and the trials were conducted to see if the concentration of sulfur, nitrogen compounds rise after dissolving.

3.3.1. Dissolution Study to Capture SO $_x$, NO $_x$, and Chlorides

Sodium bicarbonate (NaHCO $_3$) (Walawska et al. 2013; Lanzerstorfer 2017), urea (CON $_2$ H $_4$) (Aries 2011; Chun et al. 2017), and di-sodium borate deca-hydrate (Na $_2$ B $_4$ O $_7$ ·10(H $_2$ O) or Borax) were selected as they are known for high absorbance of SO $_x$ and NO $_x$. In recent times, sodium bicarbonate is preferred to sodium carbonate or CaCO $_3$ as a means of treating sinter waste gas, especially for De-SO $_x$. Borax is used in determining the ammonical nitrogen in the water and hence was selected. It was anticipated that solutions of borax, sodium bicarbonate, urea will be sprayed into wind legs.

The samples of wind leg deposits were dissolved for 24 hours in demineralized water, and 1% v/v solutions of sodium bicarbonate urea and di-sodium borate deca-hydrate to see how much SO $_x$ and NO $_x$ were dissolved. After dissolving, the solution was found to have increased levels of sulfates and nitrates. The filtrates were collected, dried, and examined under QEMSCAN. SO $_x$ and NO $_x$ were completely absent. Water and the solution of sodium bicarbonate were found to be the most effective sorbents. Hence it was planned to spray the solution of water and sodium bicarbonate into a wind box, wherein the concentration of NO $_x$ was highest. However, as the measured gas velocity in the wind box is about 105.3 m/s and flow rate of 82.77 Nm 3 /s, it was apprehended that the chances of the particulate population coming in contact with the droplets of the solution were limited.

3.3.1.1. Trial Work with Water

To see the dissolution rate of chlorides in tap water, a 3-gram sample of Wind Leg no. 7 was dissolved in 100 ml of water and left for 24 hours (to take care of the poor wettability of this dust). After filtering, the solution was found to have the properties indicated in Table 8.

Table 8
Properties of the solution, after dissolving in water

Property	After 24 Hours
pH	6.6
Conductivity Micro Siemens / cm	6658
Total Dissolved Solids (TDS), ppm	4324
Total Hardness, ppm	2171
Ca, ppm	789
Mg, ppm	49
Chloride, ppm	1373
Alkalinity, ppm	42
Ammonical Nitrogen, ppm	131
Sulfate, ppm	1990

From the above, it is evident that SO_x, NO_x got dissolved, and hence the sulfate and ammonical nitrogen have increased in the solution. Chlorides have also gone up, meaning KCl, NaCl has also be captured. The filtrate was observed under QEMSCAN and found that no salts had remained. It has Ca, Fe, O majorly. The images of the filtrate, spectra, and elemental analyses are shown in Fig. 17 to Fig. 22.

3.3.1.2. Dissolving in De-mineralised Water

Another 10 gram of sample from Wind Leg no. 7 was dissolved in 1000 ml DM water and put on a shaker for one hour and 24 hours. After filtering, the properties of the solution were measured as given in Table 9.

Table 9
Properties of the solution after dissolving in DM water

Property	After One Hour	After 24 Hours
pH	7.3	6.6
Conductivity Micro Siemens / cm	2239	2141
Total Dissolved Solids (TDS), ppm	1455	1390
Total Hardness, ppm	747	656
Ca, ppm	271	174
Mg, ppm	17	54
Chloride, ppm	325	426
Alkalinity, ppm	42	34
Ammonical Nitrogen, ppm	29	38.8
Sulfate, ppm	752	645

It is understood from the above that majority of the sulfate is dissolved within an hour. Chlorides and nitrates took more time to dissolve. The dissolution of nitrates and sulfates is far less than normal water.

3.3.1.3. Dissolving in Sodium Bicarbonate Solution

To verify the role of sodium bicarbonate, a 5-gram sample Wind Leg no. 8 was mixed with 5 grams of sodium bicarbonate and dissolved in 500 ml of DM water. It was allowed to get mixed thoroughly on a shaker for 24 hours. After filtering, the solution was characterized as given in Table 10. It is seen that most of the sulfates and some amount of chlorides got dissolved.

Table 10
Properties of the solution (sodium bicarbonate)

Property	After 24 Hours
pH	7.8
Conductivity Micro Siemens / cm	9546
Total Dissolved Solids (TDS), ppm	6205
Total Hardness, ppm	151
Ca, ppm	44
Mg, ppm	10
Chloride, ppm	263
Alkalinity, ppm	4700
Ammonical Nitrogen, ppm	-NIL-
Sulfate, ppm	1479

3.3.1.4. Dissolving in Borax Solution

The dust was dissolved in Di-Sodium Borate Deca-Hydrate and filtrate was taken out. The properties of the solution after dissolution are given in Table 11.

Table 11
Properties of the solution (borate)

Property	After 24 Hours
pH	9.3
Conductivity Micro Siemens / cm	1184
Total Dissolved Solids (TDS), ppm	769
Total Hardness, ppm	2272
Ca, ppm	796
Mg, ppm	68.5
Chloride, ppm	830
Alkalinity, ppm	4961
Ammonical Nitrogen, ppm	69.6
Sulfate, ppm	152

More amount of Ca, Mg, Chlorides got dissolved than nitrates and sulfates.

3.3.1.5. Dissolving in Urea Solution

A 15% reduction of SO_x by adding 0.02% urea in the sinter mix was reported by Eric Aries and D Poole (Aries 2011). To establish the optimum concentration, the urea content was varied as 0.1%, 1%, 5% & 10%. The dissolution data of chloride, sulfate, and ammonical nitrogen are given in Table 12.

Table 12
Properties of the solution, with varying content of urea

Property	0.10%	1%	5%	10%
pH	7.6	7.7	7.9	7.95
Conductivity Micro Siemens / cm	9329	9383	7708	7405
Total Dissolved Solids (TDS), ppm	6064	6099	5010	4813
Total Hardness, ppm	2626	2565	2060	1959
Ca, ppm	856	888	666	646
Mg, ppm	117.8	83	110	83
Chloride, ppm	2810	2748	2266	2189
Alkalinity, ppm	79.2	101	88	119
Ammonical Nitrogen, ppm	73.3	101	220	302
Sulfate, ppm	318	576	347	828

The filtrate was examined in QEMSCAN and the observations are as given below.

From the data, it is evident that urea is not only very effective for nitrates and sulfates but also chlorides. The summary is illustrated in Fig. 23. The filtrates invariably indicated reduction/absence of potassium, sodium, chlorides, sulfates, and nitrates and hence they can be removed by dissolving in water, DM water, sodium-bi-carbonate solution, urea solution, and borax solution. The residues have Ca, Mg, Si, Al, and Fe; the constituents of sinter slag. All other harmful substances had got removed, inferring that the dissolution technique was successful. However, the properties of the solution after dissolution vary and show the possibility of corrosion of steel structure/ESP electrodes. Increased NH₃ emissions were reported due to the usage of urea (Aries 2011).

From the results summarized in Fig. 23, it is evident that water, demineralized water, and sodium bicarbonate are the most effective means of removing SO_x and NO_x. Hence, the solution of water and sodium bicarbonate was tried by spraying into the wind boxes.

3.3.1.6. The Technique of Spraying in the Wind Boxes

From the dissolution studies, it was evident that SO_x, NO_x can be dissolved successfully, and hence the solution of sodium bicarbonate and water could be sprayed into wind boxes of the running sinter machine to see the breakdown of SO_x, NO_x. The arrangement of spraying the sodium bicarbonate solution into the wind box is illustrated in Fig. 24.

A solution of 0.01% v/v sodium bicarbonate in water was prepared and a pulse jet metering pump was used to spray the solution into the wind box at a rate of 2 liters per minute. A portable gas analyzer was used to monitor the NO_x level continuously. The distance between the water spray and the gas analyzer port was 2 meters and the temperature inside the wind box was 71°C during the spraying activity. The NO_x level of 556 ppm came down to 306 ppm (about 46% reduction) rapidly in about 0.06 seconds. The SO_x level reduced from 368 ppm to 20 ppm (about 94% reduction). The average SO_x, NO_x reduction rate was in the range of 55%. After increasing the concentration of sodium bicarbonate to 0.02% v/v, the reduction has increased to the 90% range.

Sodium bicarbonate was found to be an effective De-NO_x agent. It breaks down into sodium carbonate above 80 °C. Above a temperature of 120 °C, it acts as a de-sulphurising agent. Sodium carbonate de-sulphurises above 343 °C (Keener 2016; Keener and Davis 2016). Therefore, it could be used for both De-NO_x and De-SO_x in various wind boxes depending upon the temperature. This advantage eliminated the need of using sodium carbonate. 46% reduction in NO_x in 0.06 seconds and 94% reduction in SO_x was considered as significant. The kinetics of the SO_x and NO_x reduction with varying temperature and stoichiometric ratio of sodium bicarbonate in the solid-state was discussed elaborately by Walawska (Walawska et al. 2013). The NO_x removal efficiency was reported as dependant on the temperature. The highest value corresponds to 30 to 50 seconds of contact at 300 °C and the lowest at 850 °C. The same principle was adopted in the present study; and found that the kinetics were many folds higher (55% removal in 0.06 seconds).

A 500 gram of sodium bicarbonate in 50 liters of water corresponded to 0.01% v/v or 10,000 ppm. The typical NO_x particulates present in the gas were in the range of 400 ppm. The probability of the droplets of the solution coming in contact with particulates was considered fair enough. The underlying principles of SO_x, NO_x removal are given below in the form of equations (Yu et al. 2016; Ji et al. 2017a).

De-SO_x

De-NO_x

To increase the effectiveness of NO_x removal especially, the concentration was increased from 0.01% v/v to 0.02% v/v. The removal of SO_x essentially depends upon the transformation of sodium bicarbonate to sodium carbonate at temperatures above 170 °C. However, in the above experimental work, the removal of SO_x was satisfactory at temperatures in the range of 110 to 140 °C also. This was attributed to the high static pressure (-120 mBar) and velocity of the particles (Lanzerstorfer and Steiner 2016; Lanzerstorfer 2017). The summary of SO_x, NO_x reduction is given in Fig. 25. The variation of SO_x and NO_x removal with temperature was noticed to be non-linear and is indicated in Fig. 26.

Brownian Motion and Enhanced Kinetics

The rapid denitrification can be explained with the principle of Brownian Motion. Brownian motion signifies the incessant movements of particles in random directions in a solution in which the particles are much larger than the solvent molecules. Analogically, if the gas laden with NO_x particles is regarded as a continuum, the sodium bicarbonate spray can be considered as the solvent molecules. The velocity of the continuum is 20 to 100 m/s, in which the NO_x particles are also traveling. The ionic solution of sodium bicarbonate enters the wind box, get sprinkled into tiny droplets and colloid with them. However, NO_x particles have Brownian Motion. As they drift from the original path, the probability of colliding with sodium bicarbonate-laden water droplets increases. The time for the motion of sodium bicarbonate molecules is shorter

than that for the motion of NO_x particles. The particulates in the gas and the sodium bicarbonate particles move randomly following Brownian dynamics wherein collisions in the tune of 10¹² to 10²⁰ are possible.

Additionally, as the solution spreads in the wind box, the suspended particles move from higher concentration to lower concentration increasing the probability of collisions with suspended particulates in the continuum of gas. The denitrification occurs predominantly by diffusion.

3.3.2. Dissolution Study of PCDD/Fs using QEMSCAN

The alkaline compounds were found in the ESP dust, stack and also found sticking to the internals of the ESP. A puffy and light material was spotted sticking in the top of the last fields 4A and 4B of ESP, in large quantity, as shown in the location marked in Fig. 27. Its physical appearance and chemistry are shown in Fig. 28. It had compounds containing K, Cl, F, and C.

The deposition found in the ESP field 4A and 4B (Fig. 7) was examined under QEMSCAN. The chlorine present in the ESP deposit was essentially from KCl and PCDD/Fs. Based on the research of Shiu and Yu (Shiu et al. 1988b; Yu et al. 2019), 10 grams of ESP deposit was dissolved in 100 ml of acetone, hexane, and toluene. The filtrates were examined in QEMSCAN and EDAX and the results are shown in Fig. 30 to Fig. 34.

3.3.2.1. QEMSCAN of Acetone Filtrate

As seen in Fig. 31, the K and Cl are clustered and are seen as lumps, whereas the oxygen is scattered. This infers that oxygen was not present where chlorine was present or in other words, PCDD/Fs were not present after dissolving in acetone.

3.3.2.2. QEMSCAN of Hexane Filtrate

3.3.2.3. QEMSCAN of Toluene Filtrate

After dissolving the deposit in toluene (50 grams in 500 ml), the filtrate was analyzed in XRF. The oxide analysis is given in Table 13.

Table 13
Oxide analysis of filtrate (toluene)

Oxide	K ₂ O	Na ₂ O	Fe ₂ O ₃	MgO	Al ₂ O ₃	SiO ₂	SO ₃	CaO	PbO	CuO	Cl	F	LOI
Wt %	12.33	1.68	8.22	0.445	0.851	1.36	4.90	4.34	0.35	0.0395	9.01	1.00	54.72

As seen in Fig. 34, the K and Cl are ubiquitously distributed over the entire area of the image, whereas Ca and oxygen are scattered as clusters. This infers that chlorine was not present with oxygen or in other words, PCDD/Fs are not present after dissolving in toluene.

3.3.3. Dissolution study of PCDD/Fs using EDS

The filtrates obtained after dissolving in acetone, hexane, and toluene were examined under EDS and the results are given below in Fig. 35 to Fig. 39. The locations with a high amount of oxygen and chlorine were given prime consideration for detecting the presence of PCDD/Fs. The other locations had KCl and fluoride. The increased content of carbon is attributed to have come from the solvents namely acetone, hexane, and toluene. Discernment of particulates in the filtrates and vicinity of oxygen and chlorine clusters was studied using the mapping method. The location-wise elemental analysis is provided in Table 14 and Table 15. Locations 1,2,3,7 and 8 have both chlorine and oxygen in Table 14. Many locations in Table 15 have both chlorine and oxygen, indicating the possibility of PCDD/Fs. But in the mapping, chlorine, and oxygen are not at the same location. Hence it was inferred that PCDD/Fs were not present after the dissolution.

3.3.3.1. EDS of Acetone Filtrate

3.3.3.2. EDS of Hexane Filtrate

Table 14
Location-wise elemental analysis of filtrate (hexane)

Location	CK	NK	OK	FK	NaK	PK	SK	ClK	KK	CaK
1	22.15	1.50	11.70	1.58	2.56	0.18	2.52	31.38	23.90	2.52
2	22.98	0.06	13.09	0.24	0.08	0.01	4.95	25.59	27.01	5.98
3	33.99	3.05	19.98	1.98	3.12	0.39	7.32	11.68	16.16	2.32
4	10.52	1.43	46.46	23.88	0.85	0.36	1.57	4.38	3.80	6.75
5	26.70	2.35	33.40	5.91	3.19	0.41	3.32	9.94	11.93	2.85
6	45.13	3.04	22.22	2.39	2.65	0.38	4.32	6.60	11.51	1.74
7	22.23	2.17	15.21	1.81	2.60	0.23	3.61	19.95	29.72	2.48
8	14.24	1.15	22.79	11.17	2.29	0.46	3.49	12.99	12.09	19.35

3.3.3.3. EDS of Toluene Filtrate

Table 15
Location-wise elemental analysis of filtrate (toluene)

Location	CK	NK	OK	FK	NaK	AlK	SiK	PK	SK	ClK	KK	CaK	FeK
1	17.38	1.53	14.36	1.44	2.70	0.93	0.90	0.14	2.89	24.38	23.32	3.91	6.12
2	13.06	1.11	11.99	0.53	1.90	0.47	0.46	0.05	3.31	20.48	37.76	3.32	5.57
3	12.05	0.84	14.61	5.94	2.64	1.49	1.19	0.26	3.18	17.01	15.81	14.59	10.41
4	18.29	1.51	33.47	10.38	2.71	0.72	0.54	0.52	2.02	10.53	5.00	6.84	7.46
5	4.81	7.72	18.04	0.31	7.05	10.46	6.63	0.48	2.47	13.80	12.37	3.45	12.43
6	22.63	2.12	20.63	1.42	2.93	1.05	1.02	0.33	3.13	11.60	21.87	2.27	9.01
7	17.19	1.20	17.26	1.67	3.59	1.64	1.60	0.36	3.56	13.08	14.28	3.77	20.79
8	13.79	1.94	13.77	9.80	2.95	0.82	0.81	0.35	3.42	18.09	7.91	23.48	2.87
9	18.11	1.88	12.76	1.15	3.04	0.86	0.81	0.17	2.90	25.09	25.64	3.11	4.47
10	11.60	0.91	14.56	19.97	1.60	0.88	0.54	0.17	2.00	5.45	4.80	32.69	4.82
11	13.58	0.36	8.92	0.68	1.88	0.44	0.50	0.06	2.55	36.98	25.67	3.20	5.19
12	22.39	2.64	20.90	2.91	3.40	1.65	1.54	0.25	3.15	15.27	15.65	3.21	7.04
13	14.60	0.25	7.39	0.11	1.27	0.04	0.12	0.12	3.33	49.08	13.62	3.22	6.85
14	10.64	1.51	25.65	4.21	2.47	2.42	1.99	0.16	2.29	10.43	9.01	6.06	23.18
15	30.28	1.49	18.82	2.34	3.66	0.47	0.50	0.23	3.55	21.74	8.74	3.42	4.75

Prognosis of Nitrogen Injection

Since it was evident that flipping of reducing conditions to oxidizing conditions was the reason for the formation of PCDD/Fs, creating oxygen deficiency would suppress its formation. It could be abated with the help of acetone/hexane/toluene spray. However, considering the possibility of spontaneous fire in wind boxes 14,15,16, and 17 where the temperature reaches 400 °C, the injection technique was not tried. Instead, suppressing the PCDD/Fs formation by reducing oxygen is recommended such as injection of nitrogen over the sinter bed, as shown in Fig. 40.

Conclusions

The deposits found in the wind legs were due to the release of particulates, emitted from the sinter bed. Both SO_x and NO_x can be abated up to 90% by spraying 0.02% v/v sodium bicarbonate solution into wind boxes, without opting for sodium carbonate and sodium bicarbonate for addressing SO_x, NO_x separately. The removal of SO_x and NO_x with varying temperature was found to be non-linear. Simultaneous and rapid De-SO_x, De-NO_x is related to the high static pressure, gas velocity, and Brownian motion. The water present in the spray evaporates and does not pose an environmental issue. The transformation of SO_x, NO_x effectively into harmless compounds can avoid separate gas condition chamber, De-SO_x, and De-NO_x reactors, and treatment of contaminated water thereby. Characterization of the sorbent filtrates indicates the abatement of SO_x and NO_x. the breakdown of PCDD/Fs was evidenced through the characterization of acetone, hexane, and toluene filtrates. The reduction of PCDD/Fs is possible with the help of acetone, hexane, and toluene. A safe technology for spraying acetone/hexane/toluene is suggested for future development. Injecting nitrogen into wind boxes 14,15,16 and 17 to suppress PCDD/Fs formation is suggested.

Abbreviations

Borax: Di-sodium Borate Deca-hydrate

BRP: Burn-through Rise Point

BTP: Burn-through Point

BTT: Burn-through Temperature

CARB: California Air Resources Board

De-NO_x: Denitrification

De-SO_x: Desulphurization

EDS: Energy Dispersive Spectroscope

EPA: Environmental Protection Agency

ESP: Electrostatic Precipitator

FeO: Wüstite

Fe₂O₃: Hematite

LOI: Loss On Ignition

MTPA: Million Tons Per Annum

PAH: Poly Aromatic Hydrocarbons

PCDDs: Polychlorinated dibenzo para-dioxins

PCDFs: Polychlorinated dibenzofurans

PCDD/Fs: Polychlorinated dibenzo para-dioxins and polychlorinated dibenzofurans

PM_{2.5}: Particulate Matter of 2.5-micron size or below

QEMSCAN: Quantitative Evaluation of Materials by Scanning Electron Microscopy

XRD: X-Ray Diffractometer

XRF: X-Ray Fluorescence Analyzer

USEPA: United States Environmental Protection Agency

VOCs: Volatile Organic Compounds

Declarations

Ethics Approval and Consent to Participate:

There is no human and animal data in this manuscript. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for the editorial process (including Editorial Manager and direct communications with the office). He is responsible for communicating with the other authors about progress, submissions of revisions, and final approval of proofs. We confirm that we have provided a current, correct email address that is accessible by the corresponding author and which has been configured to accept email from.

Consent for Publication:

This manuscript does not contain any individual/person's data. We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property. We confirm to publish the data provided in this manuscript.

Availability of Data and Materials:

The data generated through experimentation and monitoring the performance of the sinter plants of JSW Steel Ltd, Vijayanagar Works are presented in this manuscript. We confirm that the data is an outcome of the recent research work. The Figures and Tables can be accessed with the cross-referenced hyperlinks in the manuscript. The data are available with the corresponding author. Experimental data are not available in any public domain; can be obtained from the corresponding author with permission.

Competing Interests:

We confirm that there are no known conflicts of interest associated with this publication.

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Author's Contributions:

Mr. Thimmappa Gandikoti had contributed with the analytical techniques in QMC Laboratory and Mr. Ramarao Gujare with QEMSCAN and EDS in the R&D Laboratories for characterization of the particulate deposits and the filtrates. Mr. Ramados Anbarasu had assessed the characteristics of the solutions with various sorbents in the Environmental laboratory. Dr. Srinivas Rao Raydurg and Mr. Lokendra Raj Singh had organized the resources, supervised the investigation, and validated the results. Prof. Saroj Sundar Baral supervised the entire work, guided through the manuscript writing, editing, and reviewed the research. Conceptualization, investigation, methodology, experimentation, formal analysis, and manuscript writing was done by the corresponding author Mr. Veera Brahmacharyulu Angalakuditi.

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Figures

Figure 1

Temperature in Wind Boxes & the location of the release of various particulates

Figure 2

Illustration of wind box and wind leg below the sinter machine

Figure 3

Schematic diagram of sodium bicarbonate injection in the wind legs of sinter plant

Figure 4

Dependency of stack opacity on process parameters (a) LOI, (b) Calcined Lime, (c) VM and (d) relation between Calcined Lime and Solid Fuel consumption

Figure 5

Variation of SOx, NOx in wind legs in (a) 204 m2 sinter machine, (b) 496 m2 sinter machine and variation of CO2 and O2 in (a) 204 m2 sinter machine, (b) 496 m2 sinter machine

Figure 6

Lewis structure of PCDD and PCDF

Figure 7

Graphical representation of size analysis of ESP dust

Figure 8

Morphology in Wind leg 6. Clump of (a) NO_x, (b) Crystals of NaCl and Cd, Zr particulates (wind leg 6)

Element, wt %	N	O	Mg	F	Al	Si	Cl	K	Ca	Ti	Mn	Fe	Ni	Zn	Zr	Mo	Pb	Na	P	S
1	42.25	6.33	0.77	0.00	0.44	0.00	10.69	0.37	2.17	0.00	0.05	0.48	0.64	0.58	5.27	0.00	4.16	0.00	0.00	0.00
2	14.29	2.46	0.34	0.00	0.19	0.00	11.00	0.08	0.61	0.00	0.00	0.32	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	13.90	2.72	0.71	0.00	0.42	0.00	11.23	3.63	0.17	0.01	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	12.15	2.44	0.39	0.00	0.17	0.00	11.51	0.30	0.75	0.00	0.03	0.30	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	80.06	8.13	0.90	0.00	0.46	0.10	3.22	1.52	5.96	0.00	0.00	0.47	0.31	0.09	7.57	8.87	0.86	0.00	0.00	0.00
6	85.39	7.22	1.23	2.45	0.76	0.28	9.20	1.26	5.69	0.09	0.00	0.04	0.00	0.00	8.00	12.83	0.00	0.00	0.00	0.00

Figure 9

Morphology in Wind leg 7. Crystallized (a) KCl bars and (b) NOx, KCl cubes and Zr, Pb, Mo containing particulates (wind leg 7)

Figure 10

Morphology in Wind leg 8. Pyramidal and needle-like crystals of N, S, Pb, KCl, Ca containing particulates (wind leg 8)

Element, wt %	N	O	F	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	Ni	Zn	Zr	Mo	Cd	Pb	P	S	Cl
20	26.08	3.50	0.00	0.00	0.08	0.00	0.00	4.37	11.02	0.00	0.04	3.33	1.17	0.57	0.00	23.82	42.66	1.32	0.00	0.00	0.00
21	79.93	5.21	0.00	0.00	1.09	0.48	0.01	4.07	9.89	0.06	0.30	1.50	0.73	0.73	19.75	20.89	40.22	2.94	0.00	0.00	0.00
22	38.68	3.98	0.00	0.41	0.79	0.51	0.30	4.19	11.11	0.00	0.00	2.18	0.64	0.21	0.00	23.11	41.96	0.76	0.00	0.00	0.00

Figure 11

Bar like particles containing Mo₂N, CdO, CdCO₃ (wind leg 8)

Element*	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Ni	Pb
Wt %	39.67	4.49	0.00	0.00	0.00	0.00	0.00	3.44	9.71	0.00	21.25	9.71	0.00	0.20	5.29	1.97	4.26
At %	63.43	6.28	0.00	0.00	0.00	0.00	0.00	2.49	6.78	0.00	12.17	5.43	0.00	0.08	2.12	0.75	0.46

Figure 12

PbS particulate in NOx, SOx, and K2O background (Kα Series, except Pb)

Figure 13

Mapping of N, Pb, Fe, Ca, In, Nb, Cl, Sb, Cd and Zn in a particulate, wind leg 8

Figure 14

Morphology in Wind Leg 9. Cluster of particles (A) containing KCl, NaCl, N, Ca and P, (B) containing Lead Hexaferite, PbS, PbO, PbSO₄, (C) containing CaCl₂, KCl, (D) containing NO_x, KCl, NaCl, and (E) containing Zr, Mo in NO_x background.

Figure 15

Morphology in Wind Leg 10 The deposition on its inspection door revealed the mechanism of deposition. The needle-like particles were found to impinge continuously, assimilate and appear star-like particles. Wei LV et al (Lv et al. 2018a) had reported similar micrographs. Cluster of rod (NO_x, SO_x, P2O₅), needle (CaS, PbN) and cube (NaCl) & spherical (KCl) morphologies; indicating impingement of particulates and inter-particle diffusion & assimilation

Figure 16

Cubical particulates containing NaCl, KCl, KCN, C in NOx background (wind leg 10)

Figure 17

QEMSCAN image, spectrum and elemental analysis of filtrate (water)

Figure 18

QEMSCAN image, spectrum & elemental analysis of filtrate (de-mineralized water)

Figure 19

QEMSCAN image, spectrum & elemental analysis of filtrate (sodium bicarbonate)

Figure 20

EDS mapping of filtrate (sodium bicarbonate)

Element	O	Mg	Al	Si	S	Cl	Ca	Fe	Cu
1	35.46	1.89	1.99	3.47	2.7	1.37	19.87	33.25	-
2	29.68	0.62	1.92	5.4	2.83	1.46	26.77	30.46	0.86
3	40.09	3.7	1.5	1.33	1.58	0.74	15.85	34.55	0.66

Figure 21

QEMSCAN, spectrum & elemental analysis of filtrate (Borax)

Figure 22

QEMSCAN image, spectrum & elemental analysis of filtrate (urea)

Figure 23

Summary of dissolution data

Figure 24

Schematic of spraying sodium bicarbonate solution in the wind box

Figure 25

Summary of SO_x , NO_x capture in wind legs

Figure 26

The variation of SOx, NOx removal with temperature

Figure 27

Location of sampling points in the ESP

Figure 28

Physical appearance of the deposit in 4A, 4B fields of the ESP & its chemistry

Element	O	Na	Al	Si	S	Cl	K	Ca	Fe
Wt %	13.01	4.3	0.85	0.79	3.05	34.68	30.2	5.87	7.25
At %	25.56	5.87	0.98	0.89	2.99	30.74	24.28	4.6	4.08

Element	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
Wt %	13.66	4.97	0.6	0.96	0.88	2.8	33.69	30.56	5.79	6.1
At %	26.4	6.68	0.76	1.1	0.97	2.7	29.38	24.17	4.47	3.37

Figure 29

QEMSCAN image of the deposit, spectra, and its elemental analysis

Figure 30

EDS image, spectrum & elemental analysis of filtrate (acetone)

Figure 31

Mapping of filtrate (acetone) with QEMSCAN

Figure 32

EDS image, spectrum & elemental analysis of filtrate (hexane)

Figure 33

EDS image, spectrum & elemental analysis of filtrate (toluene)

Figure 34

Mapping of filtrate (toluene) with EDS

Figure 35

Scanned area of the filtrate (acetone) & elemental analysis

Figure 36

Mapping summary of the filtrate (hexane)

Figure 37

Element-wise mapping of filtrate (hexane)

Figure 38

Mapping summary of filtrate (toluene)

Figure 39

Element-wise mapping of filtrate (toluene)

Figure 40

Schematic of sodium bicarbonate spray and nitrogen injection