

# **Coal Power Station**

**( Fly Ash , Bottom Ash & Flue Gas Desulfurization )**

**BY**

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# Fossil - fuel power station

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### - Introduction :

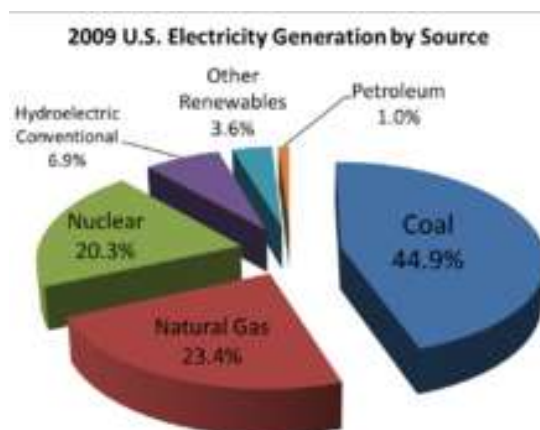
A **fossil - fuel power station** is a power station that burns fossil fuels such as coal, natural gas or petroleum (oil) to produce electricity. Central station fossil - fuel power plants are designed on a large scale for continuous operation. In many countries, such plants provide most of the electrical energy used.

Fossil fuel power stations ( except for MHD generators ) have some kind of rotating machinery to convert the heat energy of combustion into mechanical energy , which then operate an electrical generator. The prime mover may be a steam turbine, a gas turbine or,

in small isolated plants, a reciprocating internal combustion engine. All plants use the drop between the high pressure and temperature of the steam or combusting fuel and the lower pressure of the atmosphere or condensing vapour in the steam turbine.

Byproducts of power thermal plant operation need to be considered in both the design and operation. Waste heat due to the finite efficiency of the power cycle must be released to the atmosphere, using a cooling tower, or river or lake water as a cooling medium. The flue gas from combustion of the fossil fuels is discharged to the air; this contains carbon dioxide and water vapour, as well as other substances such as nitrogen, nitrogen oxides, sulfur oxides, and ( in the case of coal - fired plants ) fly ash , mercury and traces of other metals. Solid waste ash from coal-fired boilers must also be removed. Some coal ash can be recycled for building materials.

Fossil fueled power stations are major emitters of CO<sub>2</sub>, a greenhouse gas (GHG) which according to a consensus of scientific organizations is a contributor to global warming observed over the last 100 years. Brown coal emits 3 times as much CO<sub>2</sub> as natural gas, black coal emits twice as much CO<sub>2</sub> per unit of electric energy. Carbon capture and storage of emissions are not expected to be available on a commercial economically viable basis until 2025. A recent study indicates that sulfur emissions from fossil fueled power stations in China have caused a 10 - year lull in global warming (1998-2008)



*Sources of electricity in the U.S. in 2009.*

## **1 - Basic concepts ;**

In a fossil fuel power plant the chemical energy stored in fossil fuels such as coal, fuel oil, natural gas or oil shale) and oxygen of the air is converted successively into thermal energy, mechanical energy and, finally, electrical energy for continuous use and distribution across a wide geographic area. Each fossil fuel power plant is a highly complex, custom-designed system. Construction costs, as of 2004, run to US \$ 1,300 per kilo watt, or \$ 650 million for a 500 MWe unit . Multiple generating units may be built at a single site for more efficient use of land, natural resources and labour. Most thermal power stations in the world use fossil fuel, outnumbering nuclear, geothermal, biomass, or solar thermal plants.

### **1 – 1 - Heat into mechanical energy :**

The second law of thermodynamics states that any closed - loop cycle can only convert a fraction of the heat produced during combustion into mechanical work. The rest of the heat, called waste heat, must be released into a cooler environment during the return portion of the cycle. The fraction of heat released into a cooler medium must be equal or larger than the ratio of absolute temperatures of the cooling system (environment) and the heat source (combustion furnace). Raising the furnace temperature improves the efficiency but complicates the design, primarily by the selection of alloys used for construction, making the furnace more expensive. The waste heat cannot be converted into mechanical energy without an even cooler cooling system. However, it may be used in cogeneration plants to heat buildings, produce hot water, or to heat materials on an industrial scale, such as in some oil refineries, plants, and chemical synthesis plants.

Typical thermal efficiency for electrical generators in the industry is around 33 % for coal and oil-fired plants , and up to 50 % for combined - cycle gas - fired plants. Plants designed to achieve peak efficiency while operating at capacity will be less efficient when operating off - design (i.e. temperatures too low ) .

The Carnot cycle is the theoretically most efficient closed thermodynamic cycle for conversion of heat energy into useful work, and practical fossil-fuel stations cannot exceed this limit. In principle, fuel cells do not have the same thermodynamic limits as they are not heat engines.

## 2 - Fuel transport and delivery ;



*Big Bend Coal Power Station in Apollo Beach, Florida in the United States.*



*Coal fired power plants provide about 46 % of consumed electricity in the United States . This is the Castle Gate Plant near Helper, Utah.*

Coal is delivered by highway truck, rail, barge, collier ship or coal slurry pipeline. Some plants are even built near coal mines and coal is delivered by conveyors. A large coal train called a "unit train" may be two kilometers (over a mile) long, containing 100 cars with 100 short tons of coal in each one, for a total load of 10,000 tons. A large plant under full load requires at least one coal delivery this size every day. Plants may get as many as three to five trains a day, especially in "peak season" during the hottest Summer and/or coldest Winter months (depending on local climate) when power consumption is high. A large thermal power plant such as the one in Nanticoke, Ontario stores several million metric tons of coal for winter use when the lakes are frozen.

Modern unloaders use rotary dump devices, which eliminate problems with coal freezing in bottom dump cars. The unloader includes a train positioner arm that pulls the entire train to position each car over a coal hopper. The dumper clamps an individual car against a platform that swivels the car upside down to dump the coal. Swiveling couplers enable the entire operation to occur while the cars are still coupled together. Unloading a unit train takes about three hours.

Shorter trains may use railcars with an "air-dump", which relies on air pressure from the engine plus a "hot shoe" on each car. This "hot shoe" when it comes into contact with a "hot rail" at the unloading trestle, shoots an electric charge through the air dump apparatus and causes the doors on the bottom of the car to open, dumping the coal through the opening in the trestle. Unloading one of these trains takes anywhere from an hour to an hour and a half. Older unloaders may still use manually operated bottom-dump rail cars and a "shaker" attached to dump the coal. Generating stations adjacent to a mine may receive coal by conveyor belt or massive diesel-electric-drive trucks.

A collier (cargo ship carrying coal) may hold 40,000 long tons of coal and takes several days to unload. Some colliers carry their own conveying equipment to unload their own bunkers; others depend on equipment at the plant. Colliers are large, seaworthy, self-powered ships. For transporting coal in calmer waters, such as rivers and lakes, flat-bottomed vessels called barges are often used. Barges are usually unpowered and must be moved by tugboats or towboats.

For start up or auxiliary purposes, the plant may use fuel oil as well. Fuel oil can be delivered to plants by pipeline, tanker, tank car or truck. Oil is stored in vertical cylindrical steel tanks with capacities as high as 90,000 barrels (14,000 m<sup>3</sup>)' worth. The heavier no. 5 "bunker" and no. 6 fuels are typically steam - heated before pumping in cold climates.

Plants fueled by natural gas are usually built adjacent to gas transport pipelines or have dedicated gas pipelines extended to them.

### **3 - Fuel processing :**

Coal is prepared for use by crushing the rough coal to pieces less than 5 cm in size. The coal is then transported from the storage yard to in - plant storage silos by rubberized conveyor belts at rates up to 4,000 short tons per hour.

In plants that burn pulverized coal, silos feed coal pulverizers (coal mills) that take the larger 2-inch (51 mm) pieces, grind them to the consistency of face powder, sort them, and mix them with primary combustion air which transports the coal to the furnace and preheats the coal to drive off excess moisture content. A 500 M We plant may have six such pulverizers , five of which can supply coal to the furnace at 250 tons per hour under full load.

In plants that do not burn pulverized coal, the larger 2- inch (51 mm) pieces may be directly fed into the silos which then feed either mechanical distributors that drop the coal on a traveling grate or the cyclone burners, a specific kind of combustor that can efficiently burn larger pieces of fuel.

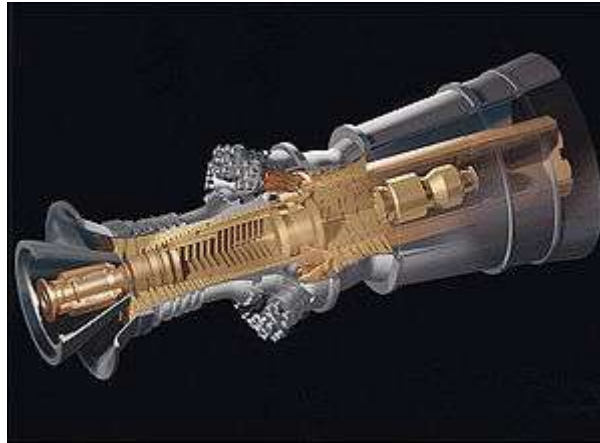
### **4 - Steam – electric :**

Most electric power made from fossil fuel is produced by thermal power stations. Reciprocating steam engines fell out of use rapidly after the first steam turbines were introduced around 1906.

### **5 - Gas turbine plants :**

One type of fossil fuel power plant uses a gas turbine in conjunction with a heat recovery steam generator (HRSG). It is referred to as a combined cycle power plant because it combines the Brayton cycle of the gas turbine with the Rankine cycle of the HRSG. The thermal efficiency of these plants has reached a record heat rate of 5690 Btu / ( kW·h ) , or just under 60 % , at a facility in Baglan Bay, Wales .





*480 megawatt GE H series power generation gas turbine*



*Currant Creek Power Plant near Mona, Utah is a natural gas fired electrical plant.*

The turbines are fueled either with natural gas, syngas or fuel oil. While more efficient and faster to construct (a 1,000 MW plant may be completed in as little as 18 months from start of construction), the economics of such plants is heavily influenced by the volatile cost of fuel, normally natural gas. The combined cycle plants are designed in a variety of configurations composed of the number of gas turbines followed by the steam turbine. For example, a 3-1 combined cycle facility has three gas turbines tied to one steam turbine. The configurations range from (1-1), (2-1), (3-1), (4-1), (5-1), to (6-1)

Simple - cycle or open cycle gas turbine plants, without a steam cycle, are sometimes installed as emergency or peaking capacity; their thermal efficiency is much lower. The high running cost per hour is offset by the low capital cost and the intention to run such units only a few hundred hours per year. Other gas turbine plants are installed in

stages, with an open cycle gas turbine the first stage and additional turbines or conversion to a closed cycle part of future project plans.

## **6 - Reciprocating engines :**

Diesel engine generator sets are often used for prime power in communities not connected to a widespread power grid. Emergency (standby) power systems may use reciprocating internal combustion engines operated by fuel oil or natural gas. Standby generators may serve as emergency power for a factory or data center, or may also be operated in parallel with the local utility system to reduce peak power demand charge from the utility. Diesel engines can produce strong torque at relatively low rotational speeds, which is generally desirable when driving an alternator, but diesel fuel in long-term storage can be subject to problems resulting from water accumulation and chemical decomposition. Rarely - used generator sets may correspondingly be installed as natural gas or LPG to minimize the fuel system maintenance requirements.

Spark-ignition internal combustion engines operating on gasoline (petrol), propane, or LPG are commonly used as portable temporary power sources for construction work, emergency power, or recreational uses.

Reciprocating external combustion engines such as the Stirling engine can be run on a variety of fossil fuels, as well as renewable fuels or industrial waste heat. Installations of Stirling engines for power production are relatively uncommon.

## **7 - Environmental impacts :**

The world's power demands are expected to rise 60 % by 2030 . With the worldwide total of active coal plants over 50,000 and rising,<sup>[8]</sup> the International Energy Agency (IEA) estimates that fossil fuels will account for 85 % of the energy market by 2030.

World organizations and international agencies, like the IEA, are concerned about the environmental impact of burning fossil fuels, and coal in particular. The combustion of coal contributes the most to

acid rain and air pollution, and has been connected with global warming. Due to the chemical composition of coal there are difficulties in removing impurities from the solid fuel prior to its combustion. Modern day coal power plants pollute less than older designs due to new "scrubber" technologies that filter the exhaust air in smoke stacks; however emission levels of various pollutants are still on average several times greater than natural gas power plants. In these modern designs, pollution from coal-fired power plants comes from the emission of gases such as carbon dioxide, nitrogen oxides, and sulfur dioxide into the air.

Acid rain is caused by the emission of nitrogen oxides and sulfur dioxide. These gases may be only mildly acidic themselves, yet when they react with the atmosphere, they create acidic compounds such as sulfurous acid, nitric acid and sulfuric acid which fall as rain, hence the term acid rain. In Europe and the U.S.A., stricter emission laws and decline in heavy industries have reduced the environmental hazards associated with this problem, leading to lower emissions after their peak in 1960s.

European Environment Agency (EEA) gives fuel-dependent emission factors based on actual emissions from power plants in EU.

<b>Pollutant</b>	<b>Hard coal</b>	<b>Brown coal</b>	<b>Fuel oil</b>	<b>Other oil</b>	<b>Gas</b>
CO <sub>2</sub> ( g / GJ )	94600	101000	77400	74100	56100
SO <sub>2</sub> ( g / GJ )	765	1361	1350	228	0.68
NO <sub>x</sub> ( g / GJ )	292	183	195	129	93.3
CO ( g / GJ )	89.1	89.1	15.7	15.7	14.5
Non methane organic compounds ( g / GJ )	4.92	7.78	3.70	3.24	1.58
Particulate matter (g / GJ )	1203	3254	16	1.91	0.1
Flue gas volume total ( m <sup>3</sup> / J )	360	444	279	276	272

## **7 – 1 - Carbon dioxide :**

Electricity generation using carbon based fuels is responsible for a large fraction of carbon dioxide (CO<sub>2</sub>) emissions worldwide and for 41% of U.S. man-made carbon dioxide emissions. Of fossil fuels, coal combustion in thermal power stations result in greater amounts of carbon dioxide emissions per unit of electricity generated ( 2249 lbs / MWh ) while oil produces less ( 1672 lb / (MW·h ) or 211 kg / GJ ) and natural gas produces the least 1135 lb / ( MW·h ) ( 143 kg / GJ ).)

The Intergovernmental Panel on Climate Change states that carbon dioxide is a greenhouse gas and that increased quantities within the atmosphere will "very likely" lead to higher average temperatures on a global scale ( global warming ) ; concerns regarding the potential for such warming to change the global climate prompted IPCC recommendations calling for large cuts to CO<sub>2</sub> emissions worldwide.

Emissions may be reduced through more efficient and higher combustion temperature and through more efficient production of electricity within the cycle. Carbon capture and storage (CCS) of emissions from coal fired power stations is another alternative but the technology is still being developed and will increase the cost of fossil fuel-based production of electricity. CCS may not be economically viable, unless the price of emitting CO<sub>2</sub> to the atmosphere rises.

## **7 – 2 - Particulate matter :**

Another problem related to coal combustion is the emission of particulates that have a serious impact on public health. Power plants remove particulate from the flue gas with the use of a bag house or electrostatic precipitator. Several newer plants that burn coal use a different process, Integrated Gasification Combined Cycle in which synthesis gas is made out of a reaction between coal and water. The synthesis gas is processed to remove most pollutants and then used initially to power gas turbines. Then the hot exhaust gases from the gas turbines are used to generate steam to power a steam turbine. The

pollution levels of such plants are drastically lower than those of "classic" coal power plants .

Particulate matter from coal - fired plants can be harmful and have negative health impacts. Studies have shown that exposure to particulate matter is related to an increase of respiratory and cardiac mortality. Particulate matter can irritate small airways in the lungs, which can lead to increased problems with asthma, chronic bronchitis, airway obstruction, and gas exchange .

There are different types of particulate matter, depending on the chemical composition and size. The dominant form of particulate matter from coal - fired plants is coal fly ash, but secondary sulfate and nitrate also comprise a major portion of the particulate matter from coal-fired plants . Coal fly ash is what remains after the coal has been combusted, so it consists of the incombustible materials that are found in the coal.

The size and chemical composition of these particles affects the impacts on human health . Currently coarse (diameter greater than  $2.5 \mu\text{m}$  ) and fine ( diameter between  $0.1 \mu\text{m}$  and  $2.5 \mu\text{m}$  ) particles are regulated, but ultrafine particles ( diameter less than  $0.1 \mu\text{m}$  ) are currently unregulated, yet they pose many dangers . Unfortunately much is still unknown as to which kinds of particulate matter pose the most harm, which makes it difficult to come up with adequate legislation for regulating particulate matter .

There are several methods of helping to reduce the particulate matter emissions from coal-fired plants. Roughly 80 % of the ash falls into an ash hopper, but the rest of the ash then gets carried into the atmosphere to become coal-fly ash . Methods of reducing these emissions of particulate matter include :

1. a bag house
2. an electrostatic precipitator ( ESP )
3. cyclone collector

The bag house has a fine filter that collects the ash particles, electrostatic precipitators use an electric field to trap ash particles on

high-voltage plates, and cyclone collectors use centrifugal force to trap particles to the walls.

### **7 – 3 - Radioactive trace elements :**

Coal is a sedimentary rock formed primarily from accumulated plant matter, and it includes many inorganic minerals and elements which were deposited along with organic material during its formation. As the rest of the Earth's crust, coal also contains low levels of uranium, thorium, and other naturally occurring radioactive isotopes whose release into the environment leads to radioactive contamination. While these substances are present as very small trace impurities, enough coal is burned that significant amounts of these substances are released. A 1,000 MW coal-burning power plant could have an uncontrolled release of as much as 5.2 metric tons per year of uranium (containing 74 pounds (34 kg) of uranium - 235) and 12.8 metric tons per year of thorium . In comparison, a 1,000 MW nuclear plant will generate about 30 short tons of high-level radioactive solid packed waste per year . It is estimated that during 1982, US coal burning released 155 times as much uncontrolled radioactivity into the atmosphere as the Three Mile Island incident . The collective radioactivity resulting from all coal burning worldwide between 1937 and 2040 is estimated to be 2,700,000 curies or 0.101 EBq . It should also be noted that during normal operation, the effective dose equivalent from coal plants is 100 times that from nuclear plants.<sup>[19]</sup> But it is also worth noting that normal operation is a deceiving baseline for comparison: just the Chernobyl nuclear disaster released, in of I-131 alone, an estimated 1,76 EBq . of radioactivity, a value one order of magnitude above this value for total emissions from all coal burned within a century. But at the same time, it shall also be understood that the <sup>131</sup> I , the major radioactive substance which comes out in accident situations has a half life of just 8 days. Hence, it is not going to cause as much as damage as the Uranium and Thorium which are released from Coal fired power plants which have much higher half lives. Also , <sup>131</sup> I can be easily removed by eating normal Iodine Tablets.

## **7 – 4 - Water and air contamination by coal ash :**

A study released in August 2010 that examined state pollution data in the United States by the organizations Environmental Integrity Project, the Sierra Club and Earth justice found that coal ash produced by coal-fired power plants dumped at sites across 21 U.S. states has contaminated ground water with toxic elements. The contaminants including the poisons arsenic and lead.

Arsenic has been shown to cause skin cancer, bladder cancer and lung cancer, and lead damages the nervous system . Coal ash contaminants are also linked to respiratory diseases and other health and developmental problems, and have disrupted local aquatic life. Coal ash also releases a variety of toxic contaminants into nearby air, posing a health threat to those who breath in fugitive coal dust.

Currently, the EPA does not regulate the disposal of coal ash; regulation is up to the states and the electric power industry has been lobbying to maintain this status quo. Most states require no monitoring of drinking water near coal ash dump sites. The study found an additional 39 contaminated U.S. sites and concluded that the problem of coal ash-caused water contamination is even more extensive in the United States than has been estimated. The study brought to 137 the number of ground water sites across the United States that are contaminated by power plant-produced coal ash .

### **7 – 4 – 1 - Range of mercury contamination in fish :**

U.S. government scientists tested fish in 291 streams around the country for mercury contamination. They found mercury in every fish tested, according to the study by the U.S. Department of the Interior. They found mercury even in fish of isolated rural waterways. Twenty five percent of the fish tested had mercury levels above the safety levels determined by the U.S. Environmental Protection Agency for people who eat the fish regularly. The largest source of mercury contamination in the United States is coal-fueled power plant emissions.

## **8 - Greening of fossil fuel power plants :**

At present, several methods exist to improve the efficiency of fossil fuel power plants. A frequently used and cost - efficient method is to convert a plant to run on a different fuel. This includes conversions as biomass and waste . Conversions to waste - fired power plants have the benefit that they can be used to eliminate existing landfills. In addition, waste fired power plants can be equipped with material recovery, allowing again additional environmental gain.

Regardless of the conversion, in order to become a truly green fossil fuel power plant, carbon capture and storage may be implemented. CCS means that the exhaust CO<sub>2</sub> is captured. This method allows any fossil fuel power plants to be converted to a emission less power plant. Examples of a CCS fossil fuel power plant includes the Elsam power station near Esbjerg, Denmark.

### **8 – 1 - Low NOx Burners :**

A common retrofit in fossil fueled power stations is the replacement of original burners with Low NOx burners. Careful consideration of fluid dynamics and flame thermodynamics has enabled substantial reduction in flame temperature, leading to reduced formation of Nitrous Oxides.

### **8 – 2 - Clean coal :**

"Clean coal" is the name attributed to a process whereby coal is chemically washed of minerals and impurities, sometimes gasified, burned and the resulting flue gases treated with steam, with the purpose of removing sulfur dioxide, and re burned so as to make the carbon dioxide in the flue gas economically recoverable. The coal industry uses the term "clean coal" to describe technologies designed to enhance both the efficiency and the environmental acceptability of coal extraction, preparation and use, but has provided no specific quantitative limits on any emissions, particularly carbon dioxide. Whereas contaminants like sulfur or mercury can be removed from coal, carbon cannot be effectively removed while still leaving a usable



fuel, and clean coal plants without carbon sequestration and storage do not significantly reduce carbon dioxide emissions. James Hansen in an open letter to U.S. President Barack Obama has advocated a "moratorium and phase-out of coal plants that do not capture and store CO<sub>2</sub>".<sup>[32]</sup> In his book *Storms of My Grandchildren*, similarly, Hansen discusses his *Declaration of Stewardship* the first principle of which requires "a moratorium on coal-fired power plants that do not capture and sequester carbon dioxide".

## **9 - Combined heat and power :**

Combined heat and power (CHP), also known as cogeneration, is the use of a power station to provide both electric power and process heat or district heating . While rejecting heat at a higher than normal temperature to enable building heating lowers overall plant electric power efficiency, the extra fuel burnt is more than offset by the reduction in fossil fuel that would otherwise be used for heating buildings . This technology is widely practiced in for example Denmark , other Scandinavian countries and parts of Germany. Calculations show that CHPDH is the cheapest method of carbon emissions reductions .

## **10 - Alternatives to fossil fuel power plants :**

Alternatives to fossil fuel power plants include nuclear power, solar power, geothermal power, wind power, tidal power, hydroelectric power (hydroelectricity) and other renewable energies (see non-carbon economy). Some of these are proven technologies on an industrial scale (i.e. nuclear, wind, tidal and hydroelectric power) others are still in prototype form.

Nuclear power, and geothermal power may be classed as heat pollutants as they add heat energy to the biosphere that would not otherwise be released. The net quantity of energy conversion within the biosphere due to the utilization of wind power, solar power, tidal power, hydroelectric power (hydroelectricity) is static and is derived from the effects of sunlight and the movement of the moon and planets. It may be argued that the net release of geothermal energy into the biosphere through volcanic activity is mitigated slightly over

time due to the draw down of heat energy by geothermal power stations. This would entail an extremely complex analysis to resolve for individual installations .

Generally, the cost of electrical energy produced by non fossil fuel burning power plants is greater than that produced by burning fossil fuels. This statement however only includes the cost to produce the electrical energy and does not take into account indirect costs associated with the many pollutants created by burning fossil fuels (e.g. increased hospital admissions due respiratory diseases caused by fine smoke particles) .

### **10 – 1 - Relative cost by generation source :**

When comparing power plant costs, it is customary to start by calculating the cost of power at the generator terminals by considering several main factors. External costs such as connections costs, the effect of each plant on the distribution grid are considered separately as an additional cost to the calculated power cost at the terminals.

Initial factors considered are :

- Capital costs (including waste disposal and decommissioning costs for nuclear energy)
- Operating and maintenance costs
- Fuel costs (for fossil fuel and biomass sources, and which may be negative for wastes)
- Likely annual hours per year run or load factor ( may be 30 % for wind energy, but 90 % for nuclear energy )
- Offset sales of heat ( for example in combined heat and power district heating ( CHP / DH ) ) .

These costs occur over the 30–50 year life of the fossil fuel power plants, using discounted cash flows. In general large fossil plants are attractive due to their low initial capital costs—typically around £ 750 – £ 1000 per kilowatt electrical compared to perhaps £1500 per kilowatt for onshore wind .

# Chimney



*The world's tallest chimney , in Ekibastuz, Kazakhstan .*

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- 5 Chimney draught or draft
- 6 Maintenance and problems
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### 1 – Introduction :

A **chimney** is a structure for venting hot flue gases or smoke from a boiler, stove, furnace or fire place to the outside atmosphere. Chimneys are typically vertical, or as near as possible to vertical, to ensure that the gases flow smoothly, drawing air into the combustion in what is known as the stack, or chimney, effect. The space inside a chimney is called a *flue*. Chimneys may be found in buildings, steam locomotives and ships. In the United States, the term **smoke stack**

( colloquially, **stack** ) is also used when referring to locomotive chimneys or ship chimneys, and the term **funnel** can also be used.

The height of chimneys plays role in their ability to transfer flue gases using stack effect , the dispersion of pollutants at higher altitude helps to ease down its influence on surroundings. In the case of chemically aggressive output, the tall chimney allows partial or complete self-neutralization of chemicals in the air before they reach the ground. The dispersion of pollutants over greater area reduces their concentrations in compliance with regulatory limits.

## **2 – History :**

Romans used tubes inside the walls to draw smoke out of bakeries but real chimneys appeared only in northern Europe in the 12th century. Industrial chimneys became common in the late 18th century. The earliest extant example of an English chimney is at the keep of Conisbrough Castle in Yorkshire, which dates from 1185 AD.

Chimneys have traditionally been built of brick, both in small and large buildings. Early chimneys were of a simple brick construction. Later chimneys were constructed by placing the bricks around tile liners. To control downdrafts venting caps (often called *chimney pots*) with a variety of designs are sometimes placed on the top of chimneys.

In the eighteenth and nineteenth centuries, the methods used to extract lead from its ore produced large amounts of toxic fumes. In the north of England, long near - horizontal chimneys were built, often more than 3 km long , which typically terminated in a short vertical chimney in a remote location where the fumes would cause less harm. Lead and silver deposits formed on the inside of these long chimneys, and periodically workers would be sent along the chimneys to scrape off these valuable deposits .

## **3 - Construction :**

Due to brick's limited ability to handle transverse loads, chimneys in houses were often built in a "stack", with a fireplace on

each floor of the house sharing a single chimney, often with such a stack at the front and back of the house. Today's central heating systems have made chimney placement less critical, and the use of non-structural gas vent pipe allows a flue gas conduit to be installed around obstructions and through walls.

In fact, many modern high-efficiency heating appliances do not require a chimney. Such appliances are typically installed near an outside wall, and a noncombustible wall thimble allows vent pipe to be run directly through the outside wall.



*Carved brick chimneys characteristic of late Gothic Tudor buildings, at Thornbury Castle, 1514*

Industrial chimneys are commonly referred to as flue gas stacks and are typically external structures, as opposed to being built into the wall of a building. They are generally located adjacent to a steam-generating boiler or industrial furnace and the gases are carried to it with ductwork. Today the use of reinforced concrete has almost entirely replaced brick as a structural component in the construction of industrial chimneys. Refractory bricks are often used as a lining, particularly if the type of fuel being burned generates flue gases containing acids. Modern industrial chimneys sometimes consist of a concrete windshield with a number of flues on the inside.

The 300 meter chimney at Sasol Three consists of a 26 metre diameter windshield with four 4.6 meter diameter concrete flues which are lined with refractory bricks built on rings of corbels spaced at 10 meter intervals. The reinforced concrete can be cast by conventional formwork or sliding formwork. The height is to ensure the pollutants are dispersed over a wider area to meet legislative or safety requirements.

#### 4 - Chimney pots :

A chimney pot is placed on top of the chimney to inexpensively extend the length of the chimney, and to improve the chimney's draft. A chimney with more than one pot on it indicates that there is more than one fireplace on different floors sharing the chimney.

A chimney cowl is placed on top of the chimney to prevent birds and squirrels from nesting in the chimney. They often feature a rain guard to keep rain from going down the chimney. A metal wire mesh is often used as a spark arrestor to minimize burning debris from rising out of the chimney and making it onto the roof. Although the masonry inside the chimney can absorb a large amount of moisture which later evaporates, rainwater can collect at the base of the chimney. Sometimes weep holes are placed at the bottom of the chimney to drain out collected water.



*Spanish Conquistador style wind directional cowl found on many homes along the windy Oregon coast.*

A chimney cowl or wind directional cap is helmet shaped chimney cap that rotates to align with the wind and prevent a backdraft of smoke and wind back down the chimney.

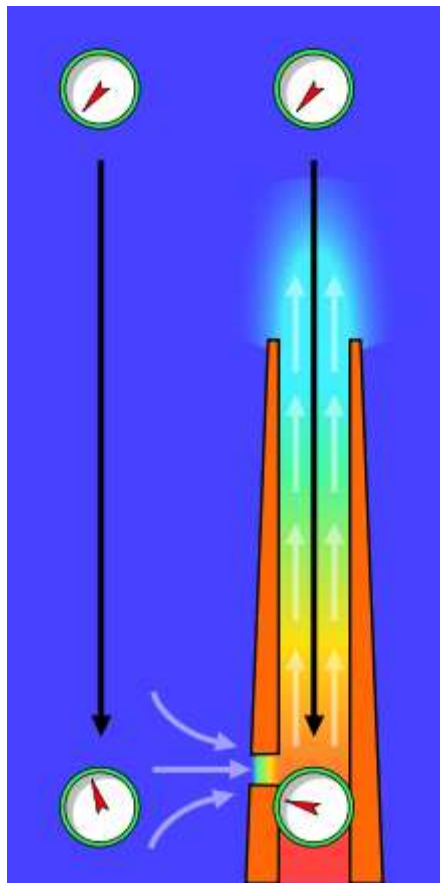
An **H - style cap** ( cowl ) is a chimney top constructed from chimney pipes shaped like the letter H. It is an age old method to regulate draft in situations where prevailing winds or turbulences cause down draft and back puffing. Although the **H cap** has a distinctive advantage over most other downdraft caps, it fell out of favor because of its bulky looks. It is found mainly in marine use but has been gaining popularity again due to its energy saving functionality. The **H - cap** stabilizes the draft rather than increasing it. Other down draft caps are based on the Venturi effect , solving

downdraft problems by increasing the up draft constantly resulting in much higher fuel consumption.

A chimney damper is a metal spring door placed at the top of the chimney with a long metal chain that allows one to open and close the chimney from the fireplace.

In the late Middle Ages in Western Europe the design of crow-stepped gables arose to allow maintenance access to the chimney top, especially for tall structures such as castles and great manor houses.

### 5 - Chimney draught or draft :



*The stack effect in chimneys: the gauges represent absolute air pressure and the airflow is indicated with light grey arrows. The gauge dials move clockwise with increasing pressure.*

When coal , oil , natural gas , wood or any other fuel is combusted in a stove, oven, fireplace, hot water boiler or industrial furnace, the hot combustion product gases that are formed are called flue gases. Those gases are generally exhausted to the

ambient outside air through chimneys or industrial flue gas stacks ( some times referred to as smoke stacks ) .

The combustion flue gases inside the chimneys or stacks are much hotter than the ambient outside air and therefore less dense than the ambient air. That causes the bottom of the vertical column of hot flue gas to have a lower pressure than the pressure at the bottom of a corresponding column of outside air. That higher pressure outside the chimney is the driving force that moves the required combustion air into the combustion zone and also moves the flue gas up and out of the chimney. That movement or flow of combustion air and flue gas is called "natural draught/draft", "natural ventilation", "chimney effect", or "stack effect". The taller the stack, the more draught or draft is created. There can be cases of diminishing returns: if a stack is overly tall in relation to the heat being sent out of the stack, the flue gases may cool before reaching the top of the chimney. This condition can result in poor drafting, and in the case of wood burning appliances, the cooling of the gases prior to exiting the chimney can cause creosote to condense near the top of the chimney. The creosote can restrict the exit of flue gases and may pose a fire hazard.

Designing chimneys and stacks to provide the correct amount of natural draught or draft involves a number design factors, many of which require iterative trial-and-error methods.

As a "first guess" approximation, the following equation can be used to estimate the natural draught/draft flow rate by assuming that the molecular mass (i.e., molecular weight) of the flue gas and the external air are equal and that the frictional pressure and heat losses are negligible :

$$Q = C A \sqrt{2 g H \frac{T_i - T_e}{T_e}}$$

**Where :**

$Q$  = chimney draught / draft flow rate , m<sup>3</sup>/s

$A$  = cross - sectional area of chimney , m<sup>2</sup>



- ( assuming it has a constant cross-section )
- $C$  = discharge coefficient ( usually taken to be from 0.65 to 0.70 )
- $g$  = gravitational acceleration,  $9.807 \text{ m / s}^2$
- $H$  = height of chimney, m
- $T_i$  = average temperature inside the chimney, K
- $T_e$  = external air temperature, K.

Combining two flows into chimney :  $A_t + A_f < A$  , where  $A_t=7.1 \text{ inch}^2$  is the minimum required flow area from water heater tank and  $A_f = 19.6 \text{ inch}^2$  is the minimum flow area from a furnace of a central heating system.

## 6 - Maintenance and problems :



*Chimneys on the Parliamentary Library in Wellington, New Zealand.*

A characteristic problem of chimneys is they develop deposits of creosote on the walls of the structure when used with wood as a fuel. Deposits of this substance can interfere with the airflow and more importantly, they are flammable and can cause dangerous chimney fires if the deposits ignite in the chimney. Thus, it is

recommended — and in some countries even mandatory — that chimneys be inspected annually and cleaned on a regular basis to prevent these problems. The workers who perform this task are called chimney sweeps. This work used to be done largely by child labour , and as such features in Victorian literature. In the Middle Ages in some parts of Europe, a crow- stepped gable design was developed, partly to provide access to chimneys without use of ladders.

Masonry (brick) chimneys have also proved particularly susceptible to crumbling during earthquakes. Government housing authorities in quake-prone cities like San Francisco and Los Angeles now recommend building new homes with stud-framed chimneys around a metal flue. Bracing or strapping old masonry chimneys has not proved to be very effective in preventing damage or injury from earthquakes. It is now possible to buy "faux - brick" facades to cover these modern chimney structures.

Liners have been standard in new construction for years, but they're lacking in old structures whose masonry has not been restored and updated. Tile liners help keep flue gases where they belong. They isolate combustible building materials from high heat, and they prevent creosote and other by- products of combustion from seeping through porous brick and mortar.

Other problems include "spalling" brick, in which moisture seeps into the brick and then freezes, cracking and flaking the brick and loosening mortar seals.



*Modernist chimneys on the Casa Milà (Barcelona, Spain), by Antonio Gaudí.*

## **7 - Dual - use chimneys :**

Some very high chimneys are used for carrying antennas of mobile phone services and low power FM / TV - transmitters. Special attention must be paid to possible corrosion problems if these antennas are near the exhaust of the chimney.

In some cases the chimneys of power stations are used also as pylons . How ever this type of construction, which is used at several power stations in the former Soviet Union, is not very common, because of corrosion problems of conductor cables.

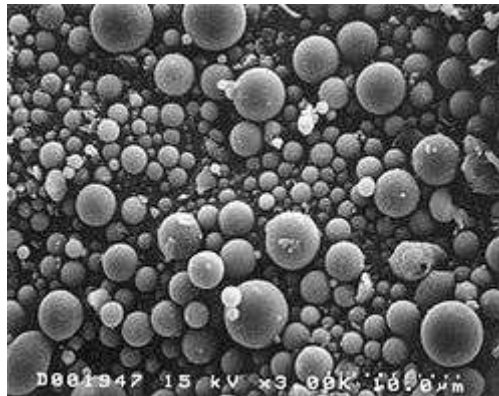
### **7 – 1 - Cooling tower used as an industrial chimney :**

At some power stations, which are equipped with plants for the removal of sulfur dioxide and nitrogen oxides, it is possible to use the cooling tower as a chimney. Such cooling towers can be seen in Germany at the Power Station Staudinger Grosskrotzenburg and at the Power Station Rostock . At power stations that are not equipped for removing sulfur dioxide, such usage of cooling towers could result in serious corrosion problems.

**8 - Notable chimneys :**

<b>Chimney</b>	<b>Year</b>	<b>Country</b>	<b>Town</b>	<b>Pinnacle height</b>	<b>Remarks</b>
GRES-2 Power Station	1987	Kazakhstan	Ekibastusz	420 m	Tallest chimney in the World
Inco Superstack	1971	Canada	Copper Cliff	385 m	
Berezovskaya GRES	1985	Russia	Sharypovo	370 m	
Trbovlje Chimney	1976	Slovenia	Trbovlje	360 m	
Sagardighi Thermal Power Station	2004	India	Sagardighi, Murshidabad	275 m	
Drax Power Station	1973	United Kingdom	Selby	259 m	
MVM Észak-Buda Power Station	1974	Hungary	Budapest	203 m	
Anaconda Smelter Stack	1919	United States of America	Anaconda, Montana	178 m	Tallest freestanding brick chimney
The Windscale Pile Chimneys	1957	United Kingdom	Windscale, Cumbria	124m	
Chimney Edstein	2008	Republic of China	Taichung, Taiwan	180 m	
Pei Tou Incinerator chimney		Taiwan	Taipei	150 m	

# Fly Ash - 1



*Photomicrograph made with a Scanning Electron Microscope (SEM):  
Fly ash particles at 2,000x magnification*

## **Contents :**

- 1 Chemical composition and classification
  - 1.1 Class F fly ash
  - 1.2 Class C fly ash
- 2 Disposal and market sources
- 3 Fly ash reuse
  - 3.1 Portland cement
  - 3.2 Embankment
  - 3.3 Soil stabilization
  - 3.4 Flow able fill
  - 3.5 Asphalt concrete
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  - 3.7 Roller compacted concrete
  - 3.8 Bricks
  - 3.9 Metal matrix composites
  - 3.10 Waste treatment and stabilization
- 4 Environmental problems
  - 4.1 Present production rate of fly ash
  - 4.2 Groundwater contamination
  - 4.3 Spills of bulk storage
  - 4.4 Contaminants
- 5 Exposure concerns

## - Introduction :

**Fly ash** is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Ash which does not rise is termed bottom ash. In an industrial context, fly ash usually refers to ash produced during combustion of coal. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipments before the flue gases reach the chimneys of coal-fired power plants, and together with bottom ash removed from the bottom of the furnace is in this case jointly known as **coal ash**. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide ( $\text{SiO}_2$ ) (both amorphous and crystalline) and calcium oxide ( $\text{CaO}$ ), both being endemic ingredients in many coal - bearing rock strata.

Toxic constituents depend upon the specific coal bed makeup, but may include one or more of the following elements or substances in quantities from trace amounts to several percent :

arsenic, beryllium, boron, cadmium, chromium, chromium VI, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium, along with dioxins and PAH compounds.

In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now require that it be captured prior to release. In the US, fly ash is generally stored at coal power plants or placed in landfills. About 43 percent is recycled, often used to supplement Portland cement in concrete production. Some have expressed health concerns about this.

In some cases, such as the burning of solid waste to create electricity ("resource recovery" facilities a.k.a. waste-to-energy facilities), the fly ash may contain higher levels of contaminants than the bottom ash and mixing the fly and bottom ash together brings the proportional levels of contaminants within the range to qualify as nonhazardous waste in a given state, whereas, unmixed, the fly ash would be within the range to qualify as hazardous waste.

## 1 - Chemical composition and classification :

Component	Bituminous	Subbituminous	Lignite
<b>SiO<sub>2</sub> (%)</b>	20-60	40-60	15-45
<b>Al<sub>2</sub>O<sub>3</sub> (%)</b>	5-35	20-30	20-25
<b>Fe<sub>2</sub>O<sub>3</sub> (%)</b>	10-40	4-10	4-15
<b>CaO (%)</b>	1-12	5-30	15-40
<b>LOI (%)</b>	0-15	0-3	0-5

Fly ash material solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5  $\mu\text{m}$  to 100  $\mu\text{m}$ . They consist mostly of silicon dioxide (SiO<sub>2</sub>), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous; aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and iron oxide (Fe<sub>2</sub>O<sub>3</sub>). Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides.

Fly ash also contains environmental toxins in significant amounts, including arsenic (43.4 ppm); barium (806 ppm); beryllium (5 ppm); boron (311 ppm); cadmium (3.4 ppm); chromium (136 ppm); chromium VI (90 ppm); cobalt (35.9 ppm); copper (112 ppm); fluorine (29 ppm); lead (56 ppm); manganese (250 ppm); nickel (77.6 ppm); selenium (7.7 ppm); strontium (775 ppm); thallium (9 ppm); vanadium (252 ppm); and zinc (178 ppm).

The above concentrations of trace elements vary according to the kind of coal burnt to form it. In fact, in the case of bituminous coal, with the notable exception of boron, trace element concentrations are generally similar to trace element concentrations in unpolluted soils.

Two classes of fly ash are defined by ASTM C618 : Class F fly ash and Class C fly ash . The chief difference between these classes is

the amount of calcium , silica , alumina , and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).

Not all fly ashes meet ASTM C 618 requirements, although depending on the application, this may not be necessary. Ash used as a cement replacement must meet strict construction standards, but no standard environmental regulations have been established in the United States . 75 % of the ash must have a fineness of 45  $\mu\text{m}$  or less, and have a carbon content, measured by the loss on ignition ( LOI ) , of less than 4 % . In the U.S., LOI needs to be under 6 % . The particle size distribution of raw fly ash is very often fluctuating constantly, due to changing performance of the coal mills and the boiler performance. This makes it necessary that, if fly ash is used in an optimal way to replace cement in concrete production, it needs to be processed using beneficiation methods like mechanical air classification. But if fly ash is used also as a filler to replace sand in concrete production, un beneficiated fly ash with higher LOI can be also used. Especially important is the ongoing quality verification. This is mainly expressed by quality control seals like the Bureau of Indian Standards mark or the DCL mark of the Dubai Municipality.

### **1 - 1 - Class F fly ash :**

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 20 % lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Alternatively, the addition of a chemical activator such as sodium silicate (water glass) to a Class F ash can lead to the formation of a geo polymer.

### **1 – 2 - Class C fly ash :**

Fly ash produced from the burning of younger lignite or sub bituminous coal, in addition to having pozzolanic properties, also has



some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20 % lime (CaO). Unlike Class F, self - cementing Class C fly ash does not require an activator. Alkali and sulfate (SO<sub>4</sub>) contents are generally higher in Class C fly ashes.

At least one US manufacturer has announced a fly ash brick containing up to 50 percent Class C fly ash. Testing shows the bricks meet or exceed the performance standards listed in ASTM C 216 for conventional clay brick; it is also within the allowable shrinkage limits for concrete brick in ASTM C 55, Standard Specification for Concrete Building Brick. It is estimated that the production method used in fly ash bricks will reduce the embodied energy of masonry construction by up to 90 %. Bricks and pavers were expected to be available in commercial quantities before the end of 2009.

## **2 - Disposal and market sources :**

In the past, fly ash produced from coal combustion was simply entrained in flue gases and dispersed into the atmosphere. This created environmental and health concerns that prompted laws which have reduced fly ash emissions to less than 1 percent of ash produced. Worldwide, more than 65 % of fly ash produced from coal power stations is disposed of in landfills and ash ponds.

The recycling of fly ash has become an increasing concern in recent years due to increasing landfill costs and current interest in sustainable development. As of 2005, U.S. coal - fired power plants reported producing 71.1 million tons of fly ash, of which 29.1 million tons were reused in various applications . If the nearly 42 million tons of unused fly ash had been recycled, it would have reduced the need for approximately 33,900,000 m<sup>3</sup> of land fill space . Other environmental benefits to recycling fly ash includes reducing the demand for virgin materials that would need quarrying and substituting for materials that may be energy-intensive to create such as Portland cement.

As of 2006, about 125 million tons of coal-combustion byproducts, including fly ash, were produced in the U.S. each year,

with about 43 percent of that amount used in commercial applications, according to the American Coal Ash Association Web site. As of early 2008, the United States Environmental Protection Agency hoped that figure would increase to 50 percent as of 2011.

### **3 - Fly ash reuse :**

There is no U.S. governmental registration or labeling of fly ash utilization in the different sectors of the economy - industry, infrastructures and agriculture. Fly ash utilization survey data, acknowledged as incomplete, are published annually by the American Coal Ash Association .

The ways of fly ash utilization include ( approximately in order of decreasing importance ) :

- Concrete production, as a substitute material for Portland cement and sand
- Embankments and other structural fills (usually for road construction)
- Grout and Flow able fill production
- Waste stabilization and solidification
- Cement clinkers production - (as a substitute material for clay)
- Mine reclamation
- Stabilization of soft soils
- Road sub base construction
- As Aggregate substitute material (e.g. for brick production)
- Mineral filler in asphaltic concrete
- Agricultural uses: soil amendment, fertilizer, cattle feeders, soil stabilization in stock feed yards, and agricultural stakes
- Loose application on rivers to melt ice<sup>[14]</sup>
- Loose application on roads and parking lots for ice control<sup>[15]</sup>
- Other applications include cosmetics, toothpaste, kitchen counter tops, floor and ceiling tiles, bowling balls, flotation devices, stucco, utensils, tool handles, picture frames, auto bodies and boat hulls, cellular concrete, geo polymers, roofing tiles, roofing granules, decking, fireplace mantles, cinder block, PVC pipe, Structural Insulated Panels, house siding and trim, running

tracks, blasting grit, recycled plastic lumber, utility poles and cross arms, railway sleepers, highway sound barriers, marine pilings, doors, window frames, scaffolding, sign posts, crypts, columns, railroad ties, vinyl flooring, paving stones, shower stalls, garage doors, park benches, landscape timbers, planters, pallet blocks, molding, mail boxes, artificial reef, binding agent, paints and under coatings, metal castings, and filler in wood and plastic products.

### **3 – 1 - Portland cement :**

Owing to its pozzolanic properties, fly ash is used as a replacement for some of the Portland cement content of concrete. The use of fly ash as a pozzolanic ingredient was recognized as early as 1914, although the earliest noteworthy study of its use was in 1937. Before its use was lost to the Dark Ages, Roman structures such as aqueducts or the Pantheon in Rome used volcanic ash (which possesses similar properties to fly ash) as pozzolan in their concrete. As pozzolan greatly improves the strength and durability of concrete, the use of ash is a key factor in their preservation.

Use of fly ash as a partial replacement for Portland cement is generally limited to Class F fly ashes. It can replace up to 30% by mass of Portland cement, and can add to the concrete's final strength and increase its chemical resistance and durability. Recently concrete mix design for partial cement replacement with High Volume Fly Ash (50 % cement replacement) has been developed. For Roller Compacted Concrete (RCC)[used in dam construction] replacement values of 70% have been achieved with processed fly ash at the Ghatghar Dam project in Maharashtra, India. Due to the spherical shape of fly ash particles, it can also increase workability of cement while reducing water demand. The replacement of Portland cement with fly ash is considered by its promoters to reduce the green house gas "foot print" of concrete, as the production of one ton of Portland cement produces approximately one ton of CO<sub>2</sub> as compared to zero CO<sub>2</sub> being produced using existing fly ash. New fly ash production, i.e., the burning of coal, produces approximately twenty to thirty tons of CO<sub>2</sub> per ton of fly ash. Since the worldwide production of Portland cement is expected to reach nearly 2 billion tons by 2010,

replacement of any large portion of this cement by fly ash could significantly reduce carbon emissions associated with construction, as long as the comparison takes the production of fly ash as a given.

### **3 – 2 - Embankment**

Fly ash properties are somewhat unique as an engineering material. Unlike typical soils used for embankment construction, fly ash has a large uniformity coefficient consisting of clay - sized particles. Engineering properties that will affect fly ash's use in embankments include grain size distribution, compaction characteristics, shear strength, compressibility, permeability, and frost susceptibility. Nearly all fly ash used in embankments are Class F fly ashes.

### **3 – 3 - Soil stabilization :**

Soil stabilization is the permanent physical and chemical alteration of soils to enhance their physical properties. Stabilization can increase the shear strength of a soil and / or control the shrink-swell properties of a soil, thus improving the load - bearing capacity of a sub-grade to support pavements and foundations. Stabilization can be used to treat a wide range of sub-grade materials from expansive clays to granular materials. Stabilization can be achieved with a variety of chemical additives including lime, fly ash, and Portland cement, as well as by - products such as lime - kiln dust (LKD) and cement - kiln dust (CKD). Proper design and testing is an important component of any stabilization project. This allows for the establishment of design criteria as well as the determination of the proper chemical additive and admixture rate to be used to achieve the desired engineering properties. Benefits of the stabilization process can include: Higher resistance (R) values, Reduction in plasticity, Lower permeability, Reduction of pavement thickness, Elimination of excavation - material hauling/handling - and base importation, Aids compaction, Provides “all-weather” access onto and within projects sites. Another form of soil treatment closely related to soil stabilization is soil modification, sometimes referred to as “mud drying” or soil conditioning. Although some stabilization inherently

occurs in soil modification, the distinction is that soil modification is merely a means to reduce the moisture content of a soil to expedite construction, whereas stabilization can substantially increase the shear strength of a material such that it can be incorporated into the project's structural design. The determining factors associated with soil modification vs soil stabilization may be the existing moisture content, the end use of the soil structure and ultimately the cost benefit provided. Equipment for the stabilization and modification processes include: chemical additive spreaders, soil mixers ( reclaimers ), portable pneumatic storage containers, water trucks, deep lift compactors, motor graders.

### **3 – 4 - Flow able fill :**

Fly ash is also used as a component in the production of flow able fill (also called controlled low strength material, or CLSM), which is used as self - leveling, self - compacting backfill material in lieu of compacted earth or granular fill. The strength of flow able fill mixes can range from 50 to 1,200 lbf / in<sup>2</sup> (0.3 to 8.3 MPa), depending on the design requirements of the project in question. Flowable fill includes mixtures of Portland cement and filler material, and can contain mineral admixtures. Fly ash can replace either the Portland cement or fine aggregate (in most cases, river sand) as a filler material. High fly ash content mixes contain nearly all fly ash, with a small percentage of Portland cement and enough water to make the mix flowable. Low fly ash content mixes contain a high percentage of filler material, and a low percentage of fly ash, Portland cement, and water. Class F fly ash is best suited for high fly ash content mixes, whereas Class C fly ash is almost always used in low fly ash content mixes.

### **3 – 5 - Asphalt concrete :**

Asphalt concrete is a composite material consisting of an asphalt binder and mineral aggregate. Both Class F and Class C fly ash can typically be used as a mineral filler to fill the voids and provide contact points between larger aggregate particles in asphalt concrete mixes. This application is used in conjunction, or as a replacement

for, other binders (such as Portland cement or hydrated lime). For use in asphalt pavement, the fly ash must meet mineral filler specifications outlined in ASTM D242. The hydrophobic nature of fly ash gives pavements better resistance to stripping. Fly ash has also been shown to increase the stiffness of the asphalt matrix, improving rutting resistance and increasing mix durability.

### **3 – 6 - Geo polymers :**

More recently, fly ash has been used as a component in geo polymers, where the reactivity of the fly ash glasses is used to generate a binder comparable to a hydrated Portland cement in appearance and properties, but with possibly reduced CO<sub>2</sub> emissions.

It should be noted that when the total carbon footprint of the alkali required to form geo polymer cement is considered, including the calcining of lime stone as an intermediate to the formation of alkali, the net reduction in total CO<sub>2</sub> emissions may be negligible. Moreover, handling of alkali can be problematic and setting of geo polymer cements is very rapid (minutes versus hours) as compared to Portland cements, making widespread use of geopolymers impractical at the ready mix level.

### **3 – 7 - Roller compacted concrete :**

Another application of using fly ash is in roller compacted concrete dams. Many dams in the US have been constructed with high fly ash contents. Fly ash lowers the heat of hydration allowing thicker placements to occur. Data for these can be found at the US Bureau of Reclamation. This has also been demonstrated in the Ghatghar Dam Project in India.

### **3 – 8 - Bricks :**

There are several techniques for manufacturing construction bricks from fly ash, producing a wide variety of products. One type of fly ash brick is manufactured by mixing fly ash with an equal amount of clay, then firing in a kiln at about 1000 degrees C. This approach has the principal benefit of reducing the amount of clay required.

Another type of fly ash brick is made by mixing soil, plaster of paris, fly ash and water, and allowing the mixture to dry. Because no heat is required, this technique reduces air pollution. More modern manufacturing processes use a greater proportion of fly ash, and a high pressure manufacturing technique, which produces high strength bricks with environmental benefits.

In the United Kingdom, fly ash has been used for over fifty years to make concrete building blocks. They are widely used for the inner skin of cavity walls. They are naturally more thermally insulating than blocks made with other aggregates .

Ash bricks have been used in house construction in Windhoek, Namibia since the 1970s. There is, however, a problem with the bricks in that they tend to fail or produce unsightly pop-outs. This happens when the bricks come into contact with moisture and a chemical reaction occurs causing the bricks to expand .

In India, fly ash bricks are used for construction. Leading manufacturers use an industrial standard known as "Pulverized fuel ash for lime - Pozzolana mixture" using over 75 % post - industrial recycled waste, and a compression process. This produces a strong product with good insulation properties and environmental benefits.

American civil engineer Henry Liu announced the invention of a new type of fly ash brick in 2007. Liu's brick is compressed at 4,000 psi and cured for 24 hours in a 66 °C steam bath, then toughened with an air entrainment agent , so that it lasts for more than 100 freeze - thaw cycles. Owing to the high concentration of calcium oxide in class C fly ash, the brick can be described as self - cementing. Since this method contains no clay and uses pressure instead of heat, it saves energy, reduces mercury pollution, and costs 20% less than traditional manufacturing techniques . This type of brick is now manufactured under license in the USA.

Some varieties of fly ash brick gain strength as they age '

### **3 – 9 - Metal matrix composites :**

Hollow fly ash can be infiltrated by molten metal to form solid, alumina encased spheres. Fly ash can also be mixed with molten metal and cast to reduce overall weight and density, due to the low density of fly ash. Research is underway to incorporate fly ash into lead acid batteries in a lead calcium tin fly ash composite in an effort to reduce weight of the battery.

### **3 – 10 - Waste treatment and stabilization :**

Fly ash, in view of its alkalinity and water absorption capacity, may be used in combination with other alkaline materials to transform sewage sludge into organic fertilizer or bio fuel.

In addition, fly ash, mainly class C, may be used in the stabilization / solidification process of hazardous wastes and contaminated soils . For example, the Rhenipal process uses fly ash as an admixture to stabilize sewage sludge and other toxic sludges. This process has been used since 1996 to stabilize large amounts of chromium(VI) contaminated leather sludges in Alcanena, Portugal.

## **4 - Environmental problems :**

### **4 – 1 - Present production rate of fly ash :**

In the United States about 131 million tons of fly ash are produced annually by 460 coal - fired power plants. A 2008 industry survey estimated that 43 percent of this ash is re-used .

### **4 – 2 – Ground water contamination :**

Since coal contains trace levels of arsenic, barium, beryllium, boron, cadmium, chromium, thallium, selenium, molybdenum and mercury, its ash will continue to contain these traces and there fore cannot be dumped or stored where rain water can leach the metals and move them to aquifers.



### **4 – 3 – Spills of bulk storage :**

Where fly ash is stored in bulk, it is usually stored wet rather than dry so that fugitive dust is minimized. The resulting impoundments (ponds) are typically large and stable for long periods, but any breach of their dams or bundling will be rapid and on a massive scale.

In December 2008 the collapse of an embankment at an impoundment for wet storage of fly ash at the Tennessee Valley Authority's Kingston Fossil Plant resulted in a major release of 5.4 million cubic yards of coal fly ash, damaging 3 homes and flowing into the Emory River. Cleanup costs may exceed \$1.2 billion. This spill was followed a few weeks later by a smaller TVA-plant spill in Alabama, which contaminated Widows Creek and the Tennessee River.

### **4 – 4 – Contaminants :**

Fly ash contains trace concentrations of heavy metals and other substances that are known to be detrimental to health in sufficient quantities. Potentially toxic trace elements in coal include arsenic, beryllium, cadmium, barium, chromium, copper, lead, mercury, molybdenum, nickel, radium, selenium, thorium, uranium, vanadium, and zinc. Approximately 10 percent of the mass of coals burned in the United States consists of unburnable mineral material that becomes ash, so the concentration of most trace elements in coal ash is approximately 10 times the concentration in the original coal.<sup>[37]</sup> A 1997 analysis by the U.S. Geological Survey (USGS) found that fly ash typically contained 10 to 30 ppm of uranium, comparable to the levels found in some granitic rocks, phosphate rock, and black shale.

In 2000, the United States Environmental Protection Agency (EPA) said that coal fly ash did not need to be regulated as a hazardous waste. Studies by the U.S. Geological Survey and others of radioactive elements in coal ash have concluded that fly ash compares with common soils or rocks and should not be the source of alarm. However, community and environmental organizations have

documented numerous environmental contamination and damage concerns.

A revised risk assessment approach may change the way coal combustion wastes (CCW) are regulated, according to an August 2007 EPA notice in the Federal Register. In June 2008, the U.S. House of Representatives held an oversight hearing on the Federal government's role in addressing health and environmental risks of fly ash.

### **5 - Exposure concerns :**

Crystalline silica and lime along with toxic chemicals are among the exposure concerns. Although industry has claimed that fly ash is "neither toxic nor poisonous," this is disputed. Exposure to fly ash through skin contact, inhalation of fine particle dust and drinking water may well present health risks. The National Academy of Sciences noted in 2007 that "the presence of high contaminant levels in many CCR (coal combustion residue) leachates may create human health and ecological concerns "

Fine crystalline silica present in fly ash has been linked with lung damage, in particular silicosis. OSHA allows  $0.10 \text{ mg/m}^3$ , (one ten-thousandth of a gram per cubic meter of air).

Another fly ash component of some concern is lime (CaO). This chemical reacts with water ( $\text{H}_2\text{O}$ ) to form calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], giving fly ash a pH some where between 10 and 12, a medium to strong base. This can also cause lung damage if present in sufficient quantities.

In a study by NIOSH at a cement company, crystalline silica exposures from fly ash were determined to be of no concern. For maintaining a safe workplace emphasis must be placed on maintaining low nuisance dust levels and to use the appropriate personal protective equipment (PPE). The conclusion of this NIOSH study is supported by other studies devoted to the effects of fly ash on the health of workers in power plants. According to these studies, fly ash dust should not be considered as "silicotic dust", because most of

the crystalline silica is coated by amorphic alumino - silicates (glass), the main constituent of fly ash particles. This was shown particularly on the basis of scanning electron microscopy observations, by a research work performed in the Netherlands, but similar findings were obtained also in other countries.

## Fly Ash -2

Fly ash is the finest of coal ash particles. It is called "fly" ash because it is transported from the combustion chamber by exhaust gases. Fly ash is the fine powder formed from the mineral matter in coal, consisting of the noncombustible matter in coal plus a small amount of carbon that remains from incomplete combustion. Fly ash is generally light tan in color and consists mostly of silt-sized and clay - sized glassy spheres. This gives fly ash a consistency somewhat like talcum powder. Properties of fly ash vary significantly with coal composition and plant - operating conditions.

Fly ash can be referred to as either cementitious or pozzolanic. A cementitious material is one that hardens when mixed with water. A pozzolanic material will also harden with water but only after activation with an alkaline substance such as lime. These cementitious and pozzolanic properties are what make some fly ashes useful for cement replacement in concrete and many other building applications.



### ***BOTTOM ASH***

Coal bottom ash and fly ash are quite different physically, mineralogically, and chemically. Bottom ash is a coarse, granular, incombustible byproduct that is collected from the bottom of furnaces that burn coal for the generation of steam, the production of electric power, or both. Bottom ash is coarser than fly ash, with grain sizes spanning from fine sand to fine gravel. The type of byproduct produced depends on the type of furnace used to burn the coal.



### ***BOILER SLAG***

Boiler slag is coarser than conventional fly ash and is formed in cyclone boilers, which produce a molten ash that is cooled with water. Boiler slag is generally a black granular material with numerous engineering uses.



### ***FGD GYPSUM***

Flue gas desulfurization (FGD) gypsum is also known as scrubber gypsum. FGD gypsum is the by product of an air pollution control system that removes sulfur from the flue gas in calcium - based scrubbing systems . It is produced by employing forced oxidation in the scrubber and is composed mostly of calcium sulfate. FGD gypsum is most commonly used for agricultural purposes and for wall board production.



*Photos courtesy of the American Coal Ash Association.*

# Electrostatic precipitator



*Electrostatic precipitator of a bio mass heating system  
with a heat power of 2 MW*

## Contents

- 1 Invention of the electrostatic precipitator
- 2 The plate precipitator
  - 2.1 Collection efficiency (R)
- 3 Modern industrial electrostatic precipitators
- 4 Wet electrostatic precipitator
- 5 Consumer-oriented electrostatic air cleaners

### - Introduction :

An **electrostatic precipitator (ESP)**, or **electrostatic air cleaner** is a particulate collection device that removes particles from a flowing gas (such as air) using the force of an induced electrostatic charge. Electrostatic precipitators are highly efficient filtration devices that minimally impede the flow of gases through the device, and can easily remove fine particulate matter such as dust and smoke from the air stream. In contrast to wet scrubbers which apply energy directly to the flowing fluid medium, an ESP applies energy only to the particulate matter being collected and therefore is very efficient in its consumption of energy (in the form of electricity).

### 1 - Invention of the electrostatic precipitator :

The first use of corona discharge to remove particles from an aerosol was by Hohlfeld in 1824. However, it was not commercialized until almost a century later. In 1907 Dr. Frederick G.

Cottrell applied for a patent on a device for charging particles and then collecting them through electrostatic attraction — the first electrostatic precipitator. He was then a professor of chemistry at the University of California, Berkeley. Cottrell first applied the device to the collection of sulfuric acid mist and lead oxide fume emitted from various acid-making and smelting activities. Vineyards in northern California were being adversely affected by the lead emissions.

At the time of Cottrell's invention, the theoretical basis for operation was not understood. The operational theory was developed later in the 1920s, in Germany.

Prof. Cottrell used proceeds from his invention to fund scientific research through the creation of a foundation called Research Corporation in 1912 to which he assigned the patents. The intent of the organization was to bring inventions made by educators (such as Cottrell) into the commercial world for the benefit of society at large. The operation of Research Corporation is perpetuated by royalties paid by commercial firms after commercialization occurs. Research Corporation has provided vital funding to many scientific projects: Goddard's rocketry experiments, Lawrence's cyclotron, production methods for vitamins A and B<sub>1</sub>, among many others. By a decision of the U.S. Supreme Court the Corporation had to be split into two entities, the Research Corporation and two commercial firms making the hardware: Research-Cottrell Inc. (operating east of the Mississippi River) and Western Precipitation operating in the Western states. The Research Corporation continues to be active to this day and the two companies formed to commercialize the invention for industrial and utility applications are still in business as well.

Electrophoresis is the term used for migration of gas-suspended charged particles in a direct-current electrostatic field. If your television set accumulates dust on the face it is because of this phenomenon (a CRT is a direct-current machine operating at about 35kV).

## **2 - The plate precipitator :**

The most basic precipitator contains a row of thin vertical wires, and followed by a stack of large flat metal plates oriented vertically, with the plates typically spaced about 1 cm to 18 cm apart, depending on the application. The air or gas stream flows horizontally through the spaces between the wires, and then passes through the stack of plates.

A negative voltage of several thousand volts is applied between wire and plate. If the applied voltage is high enough an electric (corona) discharge ionizes the gas around the electrodes. Negative ions flow to the plates and charge the gas-flow particles.

The ionized particles, following the negative electric field created by the power supply, move to the grounded plates.

Particles build up on the collection plates and form a layer. The layer does not collapse, thanks to electrostatic pressure (given from layer resistivity, electric field, and current flowing in the collected layer).

### **2 – 1 - Collection efficiency ( $R$ ) :**

Precipitator performance is very sensitive due to two particulate properties :

- 1) Resistivity; and
- 2) Particle size distribution.

These properties can be determined economically and accurately in the laboratory. A widely taught concept to calculate the collection efficiency is the Deutsch model, which assumes infinite remixing of the particles perpendicular to the gas stream.

Resistivity can be determined as a function of temperature in accordance with IEEE Standard 548. This test is conducted in an air environment containing a specified moisture concentration. The test is run as a function of ascending or descending temperature or both. Data are acquired using an average ash layer electric field of 4 kV/cm. Since relatively low applied voltage is used and no sulfuric acid vapor



is present in the environment, the values obtained indicate the maximum ash resistivity.

Usually the descending temperature test is suggested when no unusual circumstances are involved. Before the test, the ash is thermally equilibrated in dry air at 454 °C for about 14 hours. It is believed that this procedure anneals the ash and restores the surface to pre - collection condition.

If there is a concern about the effect of combustibles, the residual effect of a conditioning agent other than sulfuric acid vapor, or the effect of some other agent that inhibits the reaction of the ash with water vapor, the combination of the ascending and descending test mode is recommended. The thermal treatment that occurs between the two test modes is capable of eliminating the foregoing effects. This results in ascending and descending temperature resistivity curves that show a hysteresis related to the presence and removal of some effect such as a significant level of combustibles.

With particles of high resistivity (cement dust for example) Sulfur trioxide is sometimes injected into a flue gas stream to lower the resistivity of the particles in order to improve the collection efficiency of the electrostatic precipitator .

### **3 - Modern industrial electrostatic precipitators :**

ESPs continue to be excellent devices for control of many industrial particulate emissions, including smoke from electricity-generating utilities (coal and oil fired), salt cake collection from black liquor boilers in pulp mills, and catalyst collection from fluidized bed catalytic cracker units in oil refineries to name a few. These devices treat gas volumes from several hundred thousand ACFM to 2.5 million ACFM (1,180 m<sup>3</sup>/s) in the largest coal-fired boiler applications. For a coal-fired boiler the collection is usually performed downstream of the air pre heater at about 160 °C (320 deg.F) which provides optimal resistivity of the coal-ash particles. For some difficult applications with low-sulfur fuel hot-end units have been built operating above 371 °C .

The original parallel plate-weighted wire design (described above) has evolved as more efficient (and robust) discharge electrode designs were developed, today focusing on rigid (pipe-frame) discharge electrodes to which many sharpened spikes are attached (barbed wire), maximizing corona production. Transformer-rectifier systems apply voltages of 50 – 100 kV at relatively high current densities. Modern controls, such as an automatic voltage control, minimize electric sparking and prevent arcing (sparks are quenched within 1/2 cycle of the TR set), avoiding damage to the components. Automatic plate-rapping systems and hopper-evacuation systems remove the collected particulate matter while on line, theoretically allowing ESPs to stay in operation for years at a time.

#### **4 - Wet electrostatic precipitator :**

A wet electrostatic precipitator (WESP or wet ESP) operates with saturated air streams (100 % relative humidity). WESPs are commonly used to remove liquid droplets such as sulfuric acid mist from industrial process gas streams. The WESP is also commonly used where the gases are high in moisture content, contain combustible particulate, have particles that are sticky in nature.

The preferred and most modern type of WESP is a downflow tubular design. This design allows the collected moisture and particulate to form a slurry that helps to keep the collection surfaces clean.

Plate style and upflow design WESPs are very unreliable and should not be used in applications where particulate is sticky in nature.

#### **5 - Consumer-oriented electrostatic air cleaners :**

Plate precipitators are commonly marketed to the public as air purifier devices or as a permanent replacement for furnace filters, but all have the undesirable attribute of being some what messy to clean. A negative side - effect of electrostatic precipitation devices is the production of toxic ozone and NO<sub>x</sub>. However , electrostatic precipitators offer benefits over other air purifications technologies,

such as HEPA filtration, which require expensive filters and can become "production sinks" for many harmful forms of bacteria.

The two - stage design (charging section ahead of collecting section) has the benefit of minimizing ozone production which would adversely affect health of personnel working in enclosed spaces. For shipboard engine rooms where gearboxes generate an oil fog, two-stage ESP's are used to clean the air improving the operating environment and preventing buildup of flammable oil fog accumulations. Collected oil is returned to the gear lubricating system.

With electrostatic precipitators, if the collection plates are allowed to accumulate large amounts of particulate matter, the particles can sometimes bond so tightly to the metal plates that vigorous washing and scrubbing may be required to completely clean the collection plates. The close spacing of the plates can make thorough cleaning difficult, and the stack of plates often cannot be easily disassembled for cleaning. One solution, suggested by several manufacturers, is to wash the collector plates in a dishwasher.

Some consumer precipitation filters are sold with special soak-off cleaners, where the entire plate array is removed from the precipitator and soaked in a large container overnight, to help loosen the tightly bonded particulates.

A study by the Canada Mortgage and Housing Corporation testing a variety of forced-air furnace filters found that ESP filters provided the best, and most cost-effective means of cleaning air using a forced-air system.

## Bottom Ash

**Bottom ash** refers to part of the non - combustible residues of combustion. In an industrial context, it usually refers to coal combustion and comprises traces of combustibles embedded in forming clinkers and sticking to hot side walls of a coal - burning furnace during its operation. The portion of the ash that escapes up the chimney or stack is, however, referred to as *fly ash*. The clinkers fall by themselves into the water or sometimes by poking manually, and get cooled . The clinker lumps get crushed to small sizes by clinker grinders mounted under water and fall down into a trough from where a water ejector takes them out to a sump. From there it is pumped out by suitable rotary pumps to dumping yard far away. In another arrangement a continuous link chain scrapes out the clinkers from under water and feeds them to clinker grinders outside the bottom ash hopper.

More modern systems adopt a continuous removal philosophy. Essentially, a heavy duty chain conveyor (SSC) submerged in a water trough below the furnace which quenches hot ash as it falls from the combustion chamber and removes the wet ash continuously up a de-watering slope before onward discharge into mechanical conveyors or directly to storage silos.

Alternatively bottom ash can be conveyed using the dry technology, the MAC (Magaldi Ash Cooler) System, originally introduced since mid '80s by the Italian company Magaldi Power S.p.A. and in recent years proposed also by Clyde Bergemann's DRYCON system. These systems eliminate water usage in the cooling and conveying of bottom ash. The system cools ash using only a small controlled amount of ambient air.

Bottom ash may be used as an aggregate in road construction and concrete, where it is known as furnace bottom ash (FBA), to distinguish it from incinerator bottom ash (IBA), the non-combustible elements remaining after incineration. It was also used in the making of the concrete blocks used to construct many high-rise flats in London in the 1960s.

## Flue - Gas Desulfurization ( FGD )



*Before flue gas desulfurization was installed ,  
the emissions from this power plant in New Mexico  
contained a significant amount of sulfur dioxide.*

### Contents :

- 1 Introduction
- 2 Methods
- 3 History
- 4 Sulfuric acid mist formation
- 5 FGD chemistry
  - 5.1 Basic principles
  - 5.2 Scrubbing with a basic solid or solution
    - 5.2.1 Types of wet scrubbers used in FGD
      - 5.2.1.1 Venturi - rod scrubbers
      - 5.2.1.2 Packed bed scrubbers
      - 5.2.1.3 Spray towers
    - 5.2.2 Scrubbing reagent
  - 5.3 Scrubbing with sodium sulfite solution
  - 5.4 Gas phase oxidation followed by reaction with ammonia
- 6 Facts and statistics
- 7 Alternative methods of reducing sulfur dioxide emissions

## 1- Introduction :

Sulfur dioxide is one of the elements forming acid rain. Tall flue-gas stacks disperse emissions by diluting the pollutants in ambient air and transporting them to other regions. **Flue - gas desulfurization** ( FGD ) is a technology used to remove sulfur dioxide (  $\text{SO}_2$  ) from the exhaust flue gases of fossil-fuel power plants, and chemical producers of sulphur oxides. Fossil-fuel power plants burn coal or oil to produce steam for steam turbines, which in turn drive electrical generators.

## 2 - Methods :

As stringent environmental regulations regarding  $\text{SO}_2$  emissions have been enacted in many countries,  $\text{SO}_2$  is now being removed from flue gases by a variety of methods. The below is among the common methods used :

- Wet scrubbing using a slurry of alkaline sorbent , usually lime stone or lime, or sea water to scrub gases ;
- Spray - dry scrubbing using similar sorbent slurries;
- Wet sulfuric acid process recovering sulfur in the form of commercial quality sulfuric acid ;
- SNOX Flue gas desulfurization removes sulfur dioxide, nitrogen oxides and particulates from flue gases ;
- Dry sorbent injection systems.

For a typical coal - fired power station, FGD will remove 95 percent or more of the  $\text{SO}_2$  in the flue gases.

## 3 – History :

Methods of removing sulphur dioxide from boiler and furnace exhaust gases have been studied for over 150 years. Early ideas for flue gas desulphurization were established in England around 1850.

With the construction of large scale power plants in England in the 1920s, the problems associated with large volumes of  $\text{SO}_2$  from a single site began to concern the public. The  $\text{SO}_2$  emissions problem

did not receive much attention until 1929, when the House of Lords upheld the claim of a landowner against the Barton Electricity Works of the Manchester Corporation for damages to his land resulting from SO<sub>2</sub> emissions. Shortly there after, a press campaign was launched against the erection of power plants within the confines of London. This outcry led to the imposition of SO<sub>2</sub> controls on all such power plants.

The first major FGD unit at a utility was installed in 1931 at Batter sea Station , owned by London Power Company. In 1935, an FGD system similar to that installed at Batter sea went into service at Swansea Power Station. The third major FGD system was installed in 1938 at Fulham Power Station. These three early large-scale FGD installations were abandoned during World War II. Large-scale FGD units did not reappear at utilities until the 1970s, where most of the installations occurred in the United States and Japan.

As of June 1973, there were 42 FGD units in operation, 36 in Japan and 6 in the United States, ranging in capacity from 5 MW to 250 MW. As of around 1999 and 2000, FGD units were being used in 27 countries, and there were 678 FGD units operating at a total power plant capacity of about 229 giga watts . About 45% of the FGD capacity was in the U.S., 24 % in Germany, 11 % in Japan, and 20 % in various other countries. Approximately 79 % of the units, representing about 199 giga watts of capacity, were using lime or limestone wet scrubbing. About 18 % ( or 25 giga watts ) utilized spray-dry scrubbers or sorbent injection systems.

#### **4 - Sulfuric acid mist formation :**

Fossil fuels such as coal and oil contain a significant amount of sulfur. When fossil fuels are burned, about 95 percent or more of the sulfur is generally converted to sulfur dioxide ( SO<sub>2</sub> ) . Such conversion happens under normal conditions of temperature and of oxygen present in the flue gas. How ever, there are circumstances, under which such reaction may not occur.

When flue gas has too much oxygen, the SO<sub>2</sub> further oxidizes into sulfur trioxide ( SO<sub>3</sub> ) . Too much oxygen is only one of the ways

that  $\text{SO}_3$  is formed . Gas temperature is also an important factor. At about  $800\text{ }^\circ\text{C}$ , formation of  $\text{SO}_3$  is favored. Another way that  $\text{SO}_3$  can be formed is through catalysis by metals in the fuel. Such reaction is particularly true for heavy fuel oil , where a significant amount of vanadium is present . In what ever way  $\text{SO}_3$  is formed, it does not behave like  $\text{SO}_2$  in that it forms a liquid aerosol known as sulfuric acid (  $\text{H}_2\text{SO}_4$  ) mist that is very difficult to remove. Generally , about 1 % of the sulfur dioxide will be converted to  $\text{SO}_3$ . Sulfuric acid mist is often the cause of the blue haze that often appears as the flue gas plume dissipates . Increasingly , this problem is being addressed by the use of wet electrostatic precipitators.

## **5 - FGD chemistry :**

### **5 – 1 - Basic principles :**

Most FGD systems employ two stages: one for fly ash removal and the other for  $\text{SO}_2$  removal. Attempts have been made to remove both the fly ash and  $\text{SO}_2$  in one scrubbing vessel . How ever , these systems experienced severe maintenance problems and low removal efficiency. In wet scrubbing systems, the flue gas normally passes first through a fly ash removal device, either an electrostatic precipitator or a wet scrubber, and then into the  $\text{SO}_2$  - absorber. How ever , in dry injection or spray drying operations, the  $\text{SO}_2$  is first reacted with the sorbent, and then the flue gas passes through a particulate control device.

Another important design consideration associated with wet FGD systems is that the flue gas exiting the absorber is saturated with water and still contains some  $\text{SO}_2$  . These gases are highly corrosive to any downstream equipment such as fans, ducts , and stacks . Two methods that can minimize corrosion are :

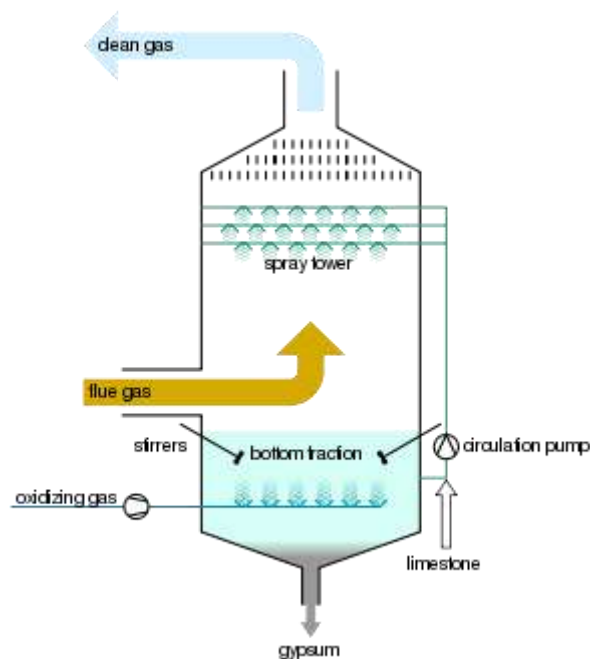
(1) reheating the gases to above their dew point , or

(2) choosing construction materials and design conditions that allow equipment to with stand the corrosive conditions.



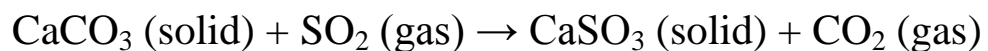
Both alternatives are expensive, and engineers designing the system determine which method to use on a site-by-site basis.

## 5 – 2 - Scrubbing with a basic solid or solution :

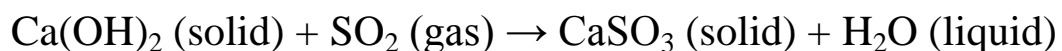


*Schematic design of the absorber of an FGD*

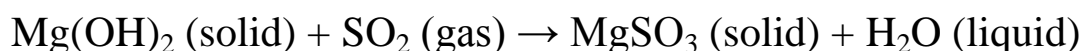
SO<sub>2</sub> is an acid gas, and , there fore, the typical sorbent slurries or other materials used to remove the SO<sub>2</sub> from the flue gases are alkaline . The reaction taking place in wet scrubbing using a CaCO<sub>3</sub> ( lime stone ) slurry produces Ca SO<sub>3</sub> ( calcium sulfite ) and can be expressed as :



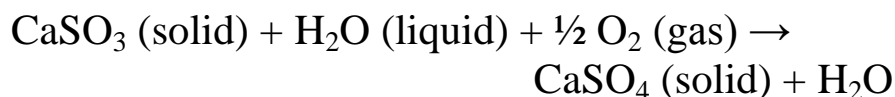
When wet scrubbing with a Ca(OH)<sub>2</sub> (lime) slurry, the reaction also produces CaSO<sub>3</sub> (calcium sulfite) and can be expressed as:



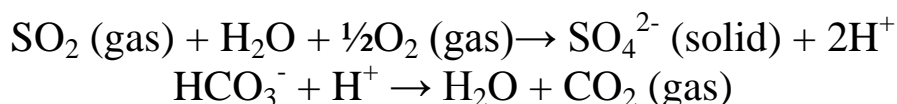
When wet scrubbing with a Mg(OH)<sub>2</sub> ( magnesium hydroxide ) slurry , the reaction produces MgSO<sub>3</sub> ( magnesium sulfite ) and can be expressed as :



To partially offset the cost of the FGD installation, in some designs, the  $\text{CaSO}_3$  (calcium sulfite) is further oxidized to produce marketable  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ( gypsum ) . This technique is also known as **forced oxidation** :



A natural alkaline usable to absorb  $\text{SO}_2$  is sea water. The  $\text{SO}_2$  is absorbed in the water, and when oxygen is added reacts to form sulfate ions  $\text{SO}_4^{2-}$  and free  $\text{H}^+$ . The surplus of  $\text{H}^+$  is offset by the carbonates in sea water pushing the carbonate equilibrium to release  $\text{CO}_2$  gas :



### 5 – 2 - 1 - Types of wet scrubbers used in FGD

To promote maximum gas - liquid surface area and residence time, a number of wet scrubber designs have been used, including spray towers , venturis , plate towers, and mobile packed beds. Because of scale buildup, plugging, or erosion, which affect FGD dependability and absorber efficiency, the trend is to use simple scrubbers such as spray towers instead of more complicated ones. The configuration of the tower may be vertical or horizontal, and flue gas can flow concurrently , counter currently , or cross currently with respect to the liquid. The chief drawback of spray towers is that they require a higher liquid - to - gas ratio requirement for equivalent  $\text{SO}_2$  removal than other absorber designs.

#### 5 – 2 - 1 – 1 - Venturi - rod scrubbers :

A venturi scrubber is a converging / diverging section of duct. The converging section accelerates the gas stream to high velocity. When the liquid stream is injected at the throat, which is the point of maximum velocity, the turbulence caused by the high gas velocity

atomizes the liquid into small droplets, which creates the surface area necessary for mass transfer to take place. The higher the pressure drop in the venturi, the smaller the droplets and the higher the surface area. The penalty is in power consumption.

For simultaneous removal of SO<sub>2</sub> and fly ash, venturi scrubbers can be used. In fact, many of the industrial sodium - based throw away systems are venturi scrubbers originally designed to remove particulate matter. These units were slightly modified to inject a sodium-based scrubbing liquor. Although removal of both particles and SO<sub>2</sub> in one vessel can be economic, the problems of high pressure drops and finding a scrubbing medium to remove heavy loadings of fly ash must be considered. However, in cases where the particle concentration is low, such as from oil-fired units, it can be more effective to remove particulate and SO<sub>2</sub> simultaneously.

### **5 – 2 - 1 – 2 - Packed bed scrubbers :**

A packed scrubber consists of a tower with packing material inside. This packing material can be in the shape of saddles, rings, or some highly specialized shapes designed to maximize contact area between the dirty gas and liquid. Packed towers typically operate at much lower pressure drops than venturi scrubbers and are therefore cheaper to operate. They also typically offer higher SO<sub>2</sub> removal efficiency. The drawback is that they have a greater tendency to plug up if particles are present in excess in the exhaust air stream.

### **5 – 2 - 1 – 3 - Spray towers**

A spray tower is the simplest type of scrubber. It consists of a tower with spray nozzles, which generate the droplets for surface contact. Spray towers are typically used when circulating a slurry (see below). The high speed of a venturi would cause erosion problems, while a packed tower would plug up if it tried to circulate a slurry.

Counter - current packed towers are infrequently used because they have a tendency to become plugged by collected particles or to scale when lime or lime stone scrubbing slurries are used.

### **5 – 2 - 2 – Scrubbing reagent :**

As explained above, alkaline sorbents are used for scrubbing flue gases to remove  $\text{SO}_2$ . Depending on the application, the two most important are lime and sodium hydroxide (also known as caustic soda). Lime is typically used on large coal or oil fired boilers as found in power plants, as it is very much less expensive than caustic soda. The problem is that it results in a slurry being circulated through the scrubber instead of a solution. This makes it harder on the equipment. A spray tower is typically used for this application. The use of lime results in a slurry of calcium sulfite ( $\text{CaSO}_3$ ) that must be disposed of. Fortunately, calcium sulfite can be oxidized to produce by-product gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which is marketable for use in the building products industry.

Caustic soda is limited to smaller combustion units because it is more expensive than lime, but it has the advantage that it forms a solution rather than a slurry. This makes it easier to operate. It produces a " spent caustic " solution of sodium sulfite / bi sulfite ( depending on the pH ), or sodium sulfate that must be disposed of . This is not a problem in a Kraft pulp mill for example, where this can be a source of make up chemicals to the recovery cycle.

### **5 – 3 - Scrubbing with sodium sulfite solution :**

It is possible to scrub sulfur dioxide by using a cold solution of sodium sulfite, this forms a sodium hydrogen sulfite solution. By heating this solution it is possible to reverse the reaction to form sulfur dioxide and the sodium sulfite solution. Since the sodium sulfite solution is not consumed, it is called a regenerative treatment. The application of this reaction is also known as the Wellman – Lord process.

In some ways this can be thought of as being similar to the reversible liquid - liquid extraction of an inert gas such as xenon or radon ( or some other solute which does not undergo a chemical change during the extraction ) from water to another phase. While a chemical change does occur during the extraction of the sulfur dioxide from the gas mixture, it is the case that the extraction

equilibrium is shifted by changing the temperature rather than by the use of a chemical reagent.

#### **5 – 4 - Gas phase oxidation followed by reaction with ammonia :**

A new, emerging flue gas desulfurization technology has been described by the IAEA . It is a radiation technology where an intense beam of electrons is fired into the flue gas at the same time as ammonia is added to the gas . The Chendu power plant in China started up such a flue gas desulfurization unit on a 100 MW scale in 1998. The Pomorzany power plant in Poland also started up a similar sized unit in 2003 and that plant removes both sulfur and nitrogen oxides. Both plants are reported to be operating successfully. However , the accelerator design principles and manufacturing quality need further improvement for continuous operation in industrial conditions.

No radioactivity is required or created in the process. The electron beam is generated by a device similar to the electron gun in a TV set. This device is called an accelerator. This is an example of a radiation chemistry process where the physical effects of radiation are used to process a substance.

The action of the electron beam is to promote the oxidation of sulfur dioxide to sulfur ( VI ) compounds. The ammonia reacts with the sulfur compounds thus formed to produce ammonium sulfate, which can be used as a nitrogenous fertilizer. In addition, it can be used to lower the nitrogen oxide content of the flue gas. This method has attained industrial plant scale .

#### **6 - Facts and statistics :**

Flue gas desulfurization scrubbers have been applied to combustion units firing coal and oil that range in size from 5 MW to 1500 MW. Scottish Power are spending £400 million installing FGD at Longannet power station, which has a capacity of over 2 GW. Dry scrubbers and spray scrubbers have generally been applied to units smaller than 300 MW.

Approximately 85 % of the flue gas desulfurization units installed in the US are wet scrubbers , 12 % are spray dry systems, and 3 % are dry injection systems.

The highest SO<sub>2</sub> removal efficiencies ( greater than 90 % ) are achieved by wet scrubbers and the lowest ( less than 80 % ) by dry scrubbers. However , the newer designs for dry scrubbers are capable of achieving efficiencies in the order of 90 %.

In spray drying and dry injection systems , the flue gas must first be cooled to about 10 – 20 °C above adiabatic saturation to avoid wet solids deposition on down stream equipment and plugging of bag houses .

The capital , operating and maintenance costs per short ton of SO<sub>2</sub> removed ( in 2001 US dollars ) are :

For wet scrubbers larger than 400 MW, the cost is \$200 to \$500 per ton

For wet scrubbers smaller than 400 MW, the cost is \$ 500 to \$ 5,000 per ton

For spray dry scrubbers larger than 200 MW, the cost is \$ 150 to \$ 300 per ton

For spray dry scrubbers smaller than 200 MW , the cost is \$ 500 to \$ 4,000 per ton

### ***Alternative methods of reducing sulfur dioxide emissions :***

An alternative to removing sulfur from the flue gases after burning is to remove the sulfur from the fuel before or during combustion. Hydro desulfurization of fuel has been used for treating fuel oils before use. Fluidized bed combustion adds lime to the fuel during combustion. The lime reacts with the SO<sub>2</sub> to form sulfates which become part of the ash.

The recently developed biological alternative Thiopaq combines gas purification with sulphur recovery. Micro - organisms in a bioreactor oxidize the sulphide to elemental sulphur. This elemental S is then separated and finally recovered at the end of the process for further usage in, for example, agricultural products. Safety is one of

the greatest benefits of this method, as the whole process takes place at atmospheric pressure and ambient temperature. This method has been developed by Paqell, a joint venture between Shell Global Solutions and Paques.

## Flue-gas emissions from fossil-fuel combustion

**Flue-gas emissions from fossil - fuel combustion** refers to the combustion product gas resulting from the much as 10 to 25 volume percent or more of the flue gas. This is closely followed in volume by water vapor ( $H_2O$ ) created by the combustion of the hydrogen in the fuel with atmospheric oxygen. Much of the 'smoke' seen pouring from flue gas stacks may in fact be water vapor forming a cloud as it contacts cool air.

A typical flue gas from the combustion of fossil fuels also contains nitrogen oxides (  $N O_x$  ), sulfur dioxide (  $SO_2$  ) and particulate matter . The nitrogen oxides are derived from the nitrogen in the ambient air as well as from any nitrogen - containing compounds in the fossil fuel . The sulfur dioxide is derived from any sulfur - containing compounds in the fuels. The particulate matter is composed of very small particles of solid materials and very small liquid droplets which give flue gases their smoky appearance.

The steam generators in large power plants and the process furnaces in large refineries , petro chemical and chemical plants, and incinerators burn large amounts of fossil fuels and there fore emit large amounts of flue gas to the atmosphere. The table below presents the total amounts of flue gas typically generated by the burning of fossil fuels such as natural gas, fuel oil and coal. Data in the table were obtained by stoichiometric calculations.

It is of interest to note that the total amount of flue gas generated by coal combustion is only 10 percent higher than the flue gas generated by natural gas combustion.



## EXHAUST FLUE GAS GENERATED BY COMBUSTION OF FOSSIL FUELS

Combustion Data	Fuel Gas	Fuel Oil	Coal
<b>Fuel properties :</b>			
Gross caloric value , MJ / m <sup>3</sup>	43.01		
Gross heating value, Btu/scf	1,093		
Gross caloric value, MJ / kg		43.50	
Gross heating value, Btu / gal		150,000	
Gross caloric value, MJ / kg			25.92
Gross heating value, Btu / lb			11,150
Molecular weight	18		
Specific gravity		0.9626	
Gravity, °API		15.5	
Carbon/hydrogen ratio by weight		8.1	
weight % carbon			61.2
weight % hydrogen			4.3
weight % oxygen			7.4
weight % sulfur			3.9
weight % nitrogen			1.2
weight % ash			12.0
weight % moisture			10.0
<b>Combustion air :</b>			
Excess combustion air , %	12	15	20
<b>Wet exhaust flue gas :</b>			
Amount of wet exhaust gas, m <sup>3</sup> / GJ of fuel	294.8	303.1	323.1
Amount of wet exhaust gas, scf/10 <sup>6</sup> Btu of fuel	11,600	11,930	12,714
CO <sub>2</sub> in wet exhaust gas , volume %	8.8	12.4	13.7
O <sub>2</sub> in wet exhaust gas , volume %	2.0	2.6	3.4
Molecular weight of wet exhaust gas	27.7	29.0	29.5
<b>Dry exhaust flue gas :</b>			
Amount of dry exhaust gas,	241.6	269.3	293.6

m<sup>3</sup> / GJ of fuel

Amount of dry exhaust gas , scf / 10 <sup>6</sup> Btu of fuel	9,510	10,600	11,554
CO <sub>2</sub> in dry exhaust gas , volume %	10.8	14.0	15.0
O <sub>2</sub> in dry exhaust gas , volume %	2.5	2.9	3.7
Molecular weight of dry exhaust gas	29.9	30.4	30.7

Note: m<sup>3</sup> are standard cubic meters at 0 °C and 101.325 kPa, and scf is standard cubic feet at 60 °F and 14.696 psia.

# Flue - gas stack

## Contents

- 1 Introduction
- 2 History
- 3 Flue - gas stack draught
- 4 The flue - gas flow - rate induced by the draught
- 5 Stack design
- 6 Other items of interest

### 1 – Introduction :

A **flue - gas stack** is a type of chimney, a vertical pipe, channel or similar structure through which combustion product gases called flue gases are exhausted to the outside air. Flue gases are produced when coal , oil , natural gas, wood or any other fuel is combusted in an industrial furnace, a power plant's steam - generating boiler, or other large combustion device. Flue gas is usually composed of carbon dioxide (  $\text{CO}_2$  ) and water vapor as well as nitrogen and excess oxygen remaining from the intake combustion air. It also contains a small percentage of pollutants such as particulate matter, carbon monoxide , nitrogen oxides and sulfur oxides . The flue gas stacks are often quite tall , up to 400 meters or more, so as to disperse the exhaust pollutants over a greater area and there by reduce the concentration of the pollutants to the levels required by governmental environmental policy and environmental regulation.

When the flue gases are exhausted from stoves, ovens, fireplaces, or other small sources within residential abodes, restaurants, hotels, or other public buildings and small commercial enterprises, their flue gas stacks are referred to as chimneys.

### 2 – History :

The first industrial chimneys were built in the mid - 17th century when it was first understood how they could improve the combustion of a furnace by increasing the draught of air into the combustion zone. As such, they played an important part in the

development of reverberatory furnaces and a coal - based metallurgical industry, one of the key sectors of the early Industrial Revolution. Most 18<sup>th</sup> - century industrial chimneys ( now commonly referred to as **flue gas stacks** ) were built into the walls of the furnace much like a domestic chimney. The first free - standing industrial chimneys were probably those erected at the end of the long condensing flues associated with smelting lead .

The powerful association between industrial chimneys and the characteristic smoke - filled landscapes of the industrial revolution was due to the universal application of the steam engine for most manufacturing processes. The chimney is part of a steam-generating boiler, and its evolution is closely linked to increases in the power of the steam engine. The chimneys of Thomas Newcomen's steam engine were incorporated into the walls of the engine house. The taller, free-standing industrial chimneys that appeared in the early 19th century were related to the changes in boiler design associated with James Watt's "double - powered" engines, and they continued to grow in stature throughout the Victorian period. Decorative embellishments are a feature of many industrial chimneys from the 1860s, with over - sailing caps and patterned brick work.

The invention of fan - assisted forced draught in the early 20th century removed the industrial chimney's original function, that of drawing air into the steam-generating boilers or other furnaces. With the replacement of the steam engine as a prime mover, first by diesel engines and then by electric motors, the early industrial chimneys began to disappear from the industrial landscape. Building materials changed from stone and brick to steel and later reinforced concrete, and the height of the industrial chimney was determined by the need to disperse combustion flue gases to comply with governmental air pollution control regulations.

### **3 - Flue - gas stack draught**

The combustion flue gases inside the flue gas stacks are much hotter than the ambient outside air and there fore less dense than the ambient air. That causes the bottom of the vertical column of hot flue

gas to have a lower pressure than the pressure at the bottom of a corresponding column of outside air. That higher pressure outside the chimney is the driving force that moves the required combustion air into the combustion zone and also moves the flue gas up and out of the chimney. That movement or flow of combustion air and flue gas is called "natural draught", "natural ventilation", "chimney effect", or "stack effect". The taller the stack, the more draught is created.

The equation below provides an approximation of the pressure difference,  $\Delta P$ , (between the bottom and the top of the flue gas stack) that is created by the draught:

$$\Delta P = C a h \left( \frac{1}{T_o} - \frac{1}{T_i} \right)$$

**Where :**

$\Delta P$  = available pressure difference, in Pa

$C$  = 0.0342

$a$  = atmospheric pressure, in Pa

$h$  = height of the flue gas stack, in m

$T_o$  = absolute outside air temperature, in K

$T_i$  = absolute average temperature of the flue gas inside the stack, in K

The above equation is an approximation because it assumes that the molar mass of the flue gas and the outside air are equal and that the pressure drop through the flue gas stack is quite small. Both assumptions are fairly good but not exactly accurate.

#### **4 - The flue - gas flow - rate induced by the draught**

As a "first guess" approximation, the following equation can be used to estimate the flue-gas flow-rate induced by the draught of a flue-gas stack. The equation assumes that the molar mass of the flue gas and the outside air are equal and that the frictional resistance and heat losses are negligible :

$$Q = C A \sqrt{2 g H \frac{T_i - T_o}{T_i}}$$

**Where :**

- $Q$**  = flue - gas flow – rate , m<sup>3</sup> / s
- $A$**  = cross - sectional area of chimney, m<sup>2</sup> ( assuming it has a constant cross – section )
- $C$**  = discharge coefficient ( usually taken to be 0.65 – 0.70 )
- $g$**  = gravitational acceleration at sea level, 9.807 m/s<sup>2</sup>
- $H$**  = height of chimney, m
- $T_i$**  = absolute average temperature of the flue gas in the stack, K
- $T_o$**  = absolute outside air temperature, K

Designing chimneys and stacks to provide the correct amount of natural draft involves a great many factors such as :

- The height and diameter of the stack.
- The desired amount of excess combustion air needed to assure complete combustion.
- The temperature of the flue gases leaving the combustion zone.
- The composition of the combustion flue gas, which determines the flue-gas density.
- The frictional resistance to the flow of the flue gases through the chimney or stack, which will vary with the materials used to construct the chimney or stack.
- The heat loss from the flue gases as they flow through the chimney or stack.
- The local atmospheric pressure of the ambient air, which is determined by the local elevation above sea level.

The calculation of many of the above design factors requires trial - and - error reiterative methods.

Government agencies in most countries have specific codes which govern how such design calculations must be performed. Many non-governmental organizations also have codes governing the design of chimneys and stacks ( notably, the ASME codes ) .

## **5 - Stack design**

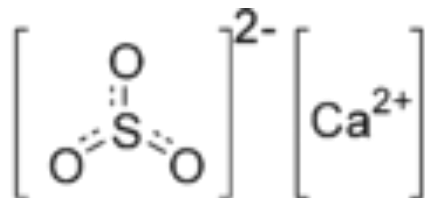
The design of large stacks poses considerable engineering challenges. Vortex shedding in high winds can cause dangerous oscillations in the stack, and may lead to its collapse. The use of helical faring is common to prevent this process occurring at or close to the resonant frequency of the stack.

## **6 - Other items of interest**

Some fuel - burning industrial equipment does not rely upon natural draught. Many such equipment items use large fans or blowers to accomplish the same objectives , namely : the flow of combustion air into the combustion chamber and the flow of the hot flue gas out of the chimney or stack.

A great many power plants are equipped with facilities for the removal of sulfur dioxide (i.e., flue gas desulfurization), nitrogen oxides (i.e., selective catalytic reduction , exhaust gas recirculation, thermal de NOx , or low NOx burners ) and particulate matter (i.e., electrostatic precipitator)s . At such power plants, it is possible to use a cooling tower as a flue gas stack. Examples can be seen in Germany at the Power Station Staudinger Grosskrotzenburg and at the Rostock Power Station. Power plants without flue gas purification, would experience serious corrosion in such stacks . In the United States and a number of other countries, atmospheric dispersion modeling studies are required to determine the flue gas stack height needed to comply with the local air pollution regulations. The United States also limits the maximum height of a flue gas stack to what is known as the "Good Engineering Practice (GEP)" stack height . In the case of existing flue gas stacks that exceed the GEP stack height, any air pollution dispersion modeling studies for such stacks must use the GEP stack height rather than the actual stack height.

## Calcium Sulfite



**Calcium sulfite**, or **calcium sulphite**, is a chemical compound which is the calcium salt of sulfurous acid with the molecular formula  $\text{CaSO}_3$ . As a food additive it is used as a preservative under the E number E226. It is commonly used in preserving wine, cider, fruit juice, canned fruit and vegetables.

Like other metal sulfites, calcium sulfite reacts with acids to produce a calcium salt, sulfur dioxide gas and water. For this reason,  $\text{CaSO}_3$  is not a desirable compound in drywall - when humid (with the natural acidity of carbon dioxide found in the air), it releases sulfur dioxide and carbon dioxide is absorbed to form calcium carbonate.

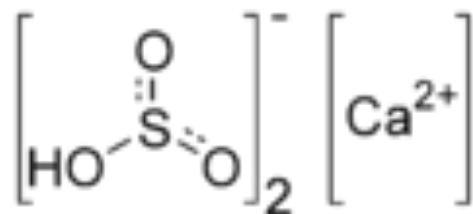
IUPAC name : Calcium sulfite

Other names : Sulfurous acid calcium salt (1:1), E226

Molecular Formula	$\text{Ca SO}_3$
Molar Mass	120 g / mol
Melting Point	600 °C
Solubility in water	0.0043 g / 100 mL , 18 °C
Flash point	Non - flammable



## Calcium bi sulfite



**Calcium bi sulfite** (calcium bi sulphite) is an inorganic compound which is the salt of a calcium cation and a bi sulfite anion. It may be prepared by reacting lime with an excess of sulfurous acid, essentially a mixture of sulfur dioxide and water. It is a weak reducing agent, as is sulfur dioxide, sulfites, and any other compound containing sulfur in the +4 oxidation state. As a food additive it is used as a preservative under the E number E227. Calcium bi sulphite is an acid salt and behaves like an acid in its aqueous solution.

IUPAC name : Calcium hydrogen sulfite

Other names : Calcium bi sulphite ,  
E227

Molecular Formula       $\text{Ca} (\text{HSO}_3)_2$

Molar Mass                      202 g / mol

# Calcium sulfate

## Contents

- 1 Introduction
- 2 Commercial production and recovery
- 3 Dehydration reactions
- 4 Fouling deposits

### 1 – Introduction :

**Calcium sulfate** (or calcium sulphate) is a common laboratory and industrial chemical. In the form of  $\gamma$  - anhydrite (the nearly anhydrous form), it is used as a desiccant. It is also used as a coagulant in products like tofu. In the natural state, unrefined calcium sulfate is a translucent, crystalline white rock. When sold as a color-indicating variant under the name Drierite , it appears blue or pink due to impregnation with Cobalt (II) chloride , which functions as a moisture indicator. The hemi hydrate ( $\text{CaSO}_4 \cdot \sim 0.5\text{H}_2\text{O}$ ) is better known as plaster of Paris, while the di hydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) occurs naturally as gypsum. The anhydrous form occurs naturally as  $\beta$ -anhydrite. Depending on the method of calcination of calcium sulfate di hydrate, specific hemihydrates are sometimes distinguished: alpha-hemi hydrate and beta- hemi hydrate. They appear to differ only in crystal size. Alpha - hemi hydrate crystals are more prismatic than beta-hemi hydrate crystals and, when mixed with water, form a much stronger and harder superstructure.

**Other names** : Plaster of Paris , Drierite , Gypsum

Molecular formula	$\text{Ca SO}_4$
	136 g / mol ( an hydrous )
Molar Mass	145 g / mol ( hemi hydrates )
	172 g / mol ( di hydrate )
Appearance	white solid
Odor	odorless
Density	2.96 g / cm <sup>3</sup> ( an hydrous )

	2.32 g / cm <sup>3</sup> ( di hydrate )
Melting point	1460°C (anhydrous)
Solubility in water	0.21 g / 100 ml at 20°C ( anhydrous )
	0.24 g / 100 ml at 20°C ( di hydrate )
Solubility product, $K_{sp}$	$4.93 \times 10^{-5}$ ( anhydrous )
	$3.14 \times 10^{-5}$ ( di hydrate )
	$3.1 \times 10^{-7}$ ( hemi hydrate )
Solubility in glycerol	slightly soluble ( di hydrate )
Acidity ( $pK_a$ )	10.4 ( anhydrous )
	7.3 ( di hydrate )
Crystal structure	orthorhombic
Flash point	Non-flammable
Thermodynamic data	Phase behaviour Solid , liquid , gas
Spectral data	UV, IR, NMR, MS

## 2 - Commercial production and recovery :

The main sources of calcium sulfate are naturally occurring gypsum and anhydrite which occur at many locations world wide as evaporates . These may be extracted by open - cast quarrying or by deep mining. World production of natural gypsum is around 127 million tones per annum.

In addition to natural sources, calcium sulfate is produced as a by-product in a number of processes:

- In flue gas desulfurization, exhaust gases from fossil-fuel-burning power stations and other processes (e.g. cement manufacture) are scrubbed to reduce their sulfur oxide content, by injecting finely ground lime stone or lime. This produces an impure calcium sulfite , which oxidizes on storage to calcium sulfate.
- In the production of phosphoric acid from phosphate rock, calcium phosphate is treated with sulfuric acid and calcium sulfate precipitates.

- In the production of hydrogen fluoride, calcium fluoride is treated with sulfuric acid, precipitating calcium sulfate.
- In the refining of zinc, solutions of zinc sulfate are treated with lime to co - precipitate heavy metals such as barium.
- Calcium sulfate can also be recovered and re - used from scrap drywall at construction sites.

These precipitation processes tend to concentrate radioactive elements in the calcium sulfate product. This is particularly the case with the phosphate by - product, since phosphate rocks naturally contain actinides.

### 3 - Dehydration reactions :

Heating gypsum to between 100 °C and 150 °C (302 °F) partially dehydrates the mineral by driving off approximately 75% of the water contained in its chemical structure. The temperature and time needed depend on ambient partial pressure of H<sub>2</sub>O. Temperatures as high as 170 °C are used in industrial calcinations , but at these temperatures  $\gamma$ - anhydrite begins to form. The reaction for the partial dehydration is:



The partially dehydrated mineral is called calcium sulfate hemi hydrate or calcined gypsum (commonly known as plaster of Paris) (CaSO<sub>4</sub>·nH<sub>2</sub>O), where n is in the range 0.5 to 0.8.

The dehydration (specifically known as calcination ) begins at approximately 80 °C , although in dry air, some dehydration will take place already at 50 °C. The heat energy delivered to the gypsum at this time (the heat of hydration) tends to go into driving off water (as water vapor) rather than increasing the temperature of the mineral, which rises slowly until the water is gone, then increases more rapidly.

The endothermic property of this reaction is exploited by drywall to confer fire resistance to residential and other structures. In a fire, the structure behind a sheet of drywall will remain

relatively cool as water is lost from the gypsum, thus preventing (or substantially retarding) damage to the framing (through combustion of wood members or loss of strength of steel at high temperatures) and consequent structural collapse.

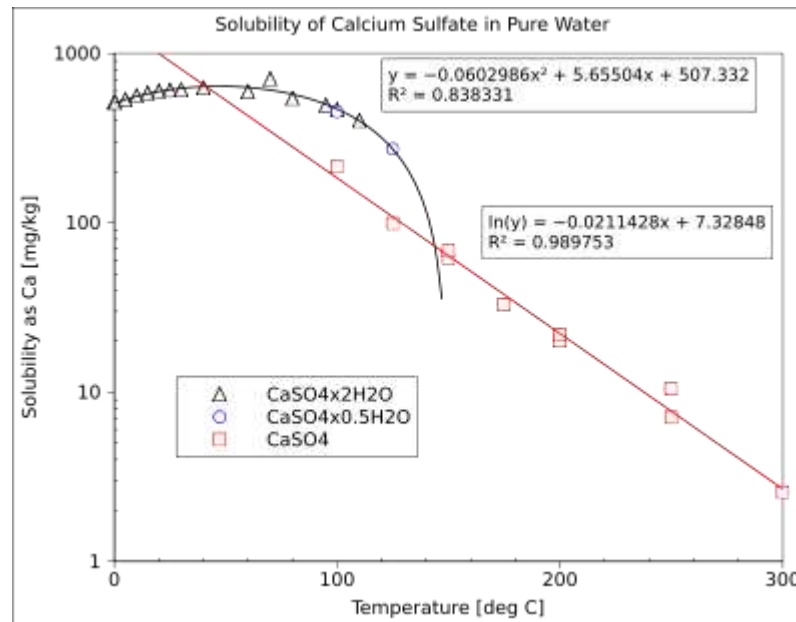
In contrast to most minerals, which when rehydrated simply form liquid or semi - liquid pastes, or remain powdery , calcined gypsum has an unusual property: when mixed with water at normal (ambient) temperatures, it quickly reverts chemically to the preferred di hydrate form, while physically "setting" to form a rigid and relatively strong gypsum crystal lattice:



This reaction is exothermic and is responsible for the ease with which gypsum can be cast into various shapes including sheets (for drywall), sticks (for blackboard chalk), and molds (to immobilize broken bones, or for metal casting). Mixed with polymers, it has been used as a bone repair cement. Small amounts of calcined gypsum are added to earth to create strong structures directly from cast earth, an alternative to adobe (which loses its strength when wet). The conditions of dehydration can be changed to adjust the porosity of the hemi hydrate, resulting in the so-called alpha and beta hemihydrates (which are more or less chemically identical).

On heating to 180 °C, the nearly water-free form, called  $\gamma$  - anhydrite ( $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  where  $n = 0$  to 0.05) is produced.  $\gamma$  - Anhydrite reacts slowly with water to return to the di hydrate state , a property exploited in some commercial desiccants. On heating above 250 °C, the completely anhydrous form called  $\beta$ -anhydrite or "natural" anhydrite is formed. Natural anhydrite does not react with water, even over geological timescales, unless very finely ground.

The variable composition of the hemihydrate and  $\gamma$ -anhydrite, and their easy inter-conversion, is due to their possessing nearly identical crystal structures, containing "channels" that can accommodate variable amounts of water, or other small molecules such as methanol.



*Temperature dependence of the solubility of calcium sulfate (3 phases) in pure water.*

#### **4 - Fouling deposits :**

Calcium sulfate is a common component of fouling deposits in industrial heat exchangers. It is because its solubility decreases with increasing temperature (see the figure).