

Advantages of novel lime technologies of concern Babcock Borsig Power Environment for flue gases desulfurization

Ryszard Kubisa, Janusz J. Kuźniar*, Artur Salamon*

Babcock Borsig Power Environment – Gummersbach, *Babcock Steinhilber Wrocław

1. Introduction

Among many desulfurization methods that are in technical use for flue gases cleaning the broadest application found methods using calcium compounds as reactants: natural limestone or processed calcium sorbents (CaO , $\text{Ca}(\text{OH})_2$).

In last few years a substantial progress was achieved in the field of waste water free desulfurization methods applied in temperature range 60 - 130 °C. It is now possible to reach efficiency higher than 90% at $\text{Ca}/\text{S} < 1.5$ or at even lower ratio in case of mechanical reactors ($\text{Ca}/\text{S} < 1.2$).

Merging of practical experience of various firms forming now concern Babcock Borsig Power caused that BBP has at its disposal several leading technologies of flue gas cleaning for every scale. For adopted partition of DeSO_x installations according to volumetric flow rate of flue gases that should be cleaned up, BBP offer contains:

- for $V_g > 1 \text{ mln Nm}^3/\text{h}$ – wet limestone method with synthetic gypsum production as a by-product,
- for $V_g \text{ 100 – 1000 thousand Nm}^3/\text{h}$ – wastewater free methods - dry scrubbing and desulfurization in circulating fluidized bed Turbosorp®,
- for $V_g < 400 \text{ thousand Nm}^3/\text{h}$ – wastewater free FHW method with mechanical reactor.

In the paper advantages of above mentioned methods were presented together with their regions of application with particular attention paid to Turbosorp® and FHW technologies. Treated here desulfurization processes do not cover desulfurization in high temperature range that takes place when sorbent is added into pulverized coal fired furnaces, or to fluidized bed boilers. In those cases desulfurization is achieved through high temperature dry process, or

such process combined with humidifying of gases outflowing from boiler before their thorough dedusting. Although these technologies are in the BBP offer too, they are not presented here due to their inferior exploitation parameters (efficiency 70 – 80%, product not suitable for further usage).

2. Wet desulfurization methods

Installations of wet desulfurization of flue gases built according to BBP **wet limestone** technology (Jaworzno III, Bełchatów, Rokita –Brzeg Dolny), work without problems and show warranted availability and efficiency. From the very beginning the economic value of synthetic gypsum production was an underestimated element of this technology in Polish market conditions. In many publications concerning wet limestone technology in early nineties (i.e. in the period of intensive introducing of this technology in the biggest power stations in Poland), synthetic gypsum overproduction was anticipated, and high additional costs of its disposal were suspected.

Today, despite of the fact that majority of big power stations are already equipped with DeSOx installations producing gypsum, demand of customers is high, and profits from its disposal are very like growing. Detailed information on the topic is not available but the exertions for increase of gypsum yield of working DeSOx installations are noticeable. Some Polish power stations are inclined to buying of coal with higher sulfur content, or to subject all flue gases stream to desulfurization. However lack of cheap unprocessed coal on the market does not allow to use the first possibility whereas the second one is connected with additional cost and technological complications.

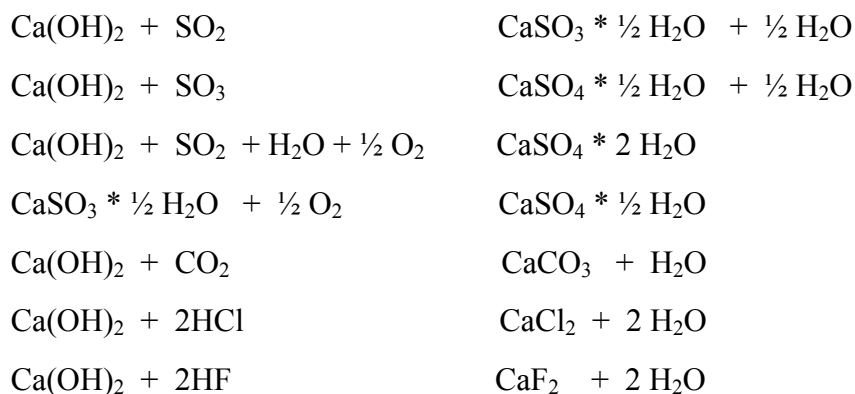
For all its advantages wet desulfurization method is inherently combined with the necessity of wastewater treatment. For not very big installations it causes diminishing of economical justification, due to high ratio of capital costs. Therefore in the last years a lot of effort was devoted to improvement of wastewater free DeSOx methods and considerable progress has been reached in the range of low temperature chemical absorption process, normally with the use of hydrated lime $\text{Ca}(\text{OH})_2$.

3. Semidry methods

Apart from known method of dry scrubbing and dry additive into furnace process in the last decade emerged new methods including isolated moistening of absorbent (being a mixture of reaction products and fresh reactant), in such a way that it keeps the properties of dry powder (having not more than 12mass % of water). This way sticking of solids to apparatus walls and corrosion were eliminated and the broad use of carbon steel in apparatus manufacturing made possible. Process regulation is much easier due to high recirculation ratios, the necessary costs involved with securing of high availability (obviously higher than energetic block itself) are also much lower than in the other technologies.

Such process is often incorrectly named „dry desulfurization” i.e. just the same as in the literature is named process in which a sorbent – mostly limestone, undergoes temperature decomposition (in the range of 750 – 900°C), and just formed CaO takes part in fixing of SO₂, SO₃, HCl, and HF. Such dry, high temperature desulfurization process, in its modification with additional moistening of dusty flue gases beyond boiler is after all in the BBP offer too, but due to its worse exploitation parameters that might be obtained is not to be characterized here.

In Turbosorp® and FHW technologies that are mainly the subject of this presentation, binding of SO₂ goes mostly in water solution according to the reactions:



Spraying of certain amount of water or water solution onto sorbent powder gives occasion to appear of tiny droplets of solution on the surface of reactant particles. In short „life time” of such droplet two main processes take place: water evaporation to gas phase having much higher temperature and in the same time lime dissolution and quick chemical reactions with acid components of gas. Particle surface temperature is then close to the temperature of adiabatic gas saturation. Product particle structure is stratified – „onion like”, connected with

multiple product recirculation, in contrast to dry scrubbing product having form of particles agglomerates of dried reaction products.

Actually have appeared some types of so called dry calcium desulfurization methods in which absorption takes place on the surface of moistened surface of sorbent. Their common advantage is simple construction of reactor in which the main process of SO₂ bonding takes place as well as taking off desulfurization product in form of powder separated from cleaned gas in conventional filtering equipment.

3.1. Turbosorp® Process

For approximately 40 years AE Energietechnik has been dealing with the design and the construction of flue gas cleaning systems. Presently, a wide range of plants is offered which are able to treat all the important flue gas pollutants like SO_x, NO_x, HCl, and HF as well as fine dusts, aerosols, dioxins, furanes, and heavy metals.

The most recent development in this field is the Turbosorp® process, where the high chemical and physical heat and mass transfer rates of a circulating fluidized-bed system are used for the elimination of the pollutants.

Together with Verbundplan the Turbosorp® process has been optimized for the desulfurization of flue gases from power stations, district heating power stations, and industrial boilers. Verbundplan is the engineering company of the Central Austrian Power Distribution Company (Verbund), who operates several flue gas cleaning plants after coal fired power stations and therefore disposes of many decades of experience in this field.

Fig.1. Scheme of Turbosorp® process

3.1.1 Process description

The flue gas desulfurization plant is arranged directly behind the boiler or a dust filter. The flue gas flows into the turbo-reactor via a venturi nozzle or a gas distributing bottom. The temperature is decreased to the optimum operating value by the injection of water in order to increase the reactivity.

In the turbo-reactor the flue gas gets in turbulent contact with the absorbent so that pollutants like SO_2 , SO_3 , HCl and HF are removed in a high extent. A minor reaction is the absorption of low amounts of carbon dioxide as well. A considerable part of the calcium sulfite having formed this way is oxidized further into calcium sulfate.

Due to the high velocities in the turbo-reactor the solids are discharged at the head of the reactor and separated in the directly adjoining dust filter. The filters are specially designed electrostatic precipitators or fabric filters which both are provided with an integrated upstream mechanical pre-separation unit.

Clean gas, that has been dedusted to the legally prescribed limit values in the dust filter is led into the stack by means of the ID-fan.

Reheating is not necessary as the clean gas temperature is approx. 80 to 100°C, and in any case it is at least 20°C above the water dew point.

In order to allow the operation of the reactor even at low boiler loads, i.e. at raw gas flows of <50% part of the clean gas has to be recirculated.

A major part of the solids eliminated by the dust filter is led back from an intermediate tank into the turboreactor by means of fluidizing conveyors. Therefore residence times of almost any required duration can be achieved and, what is characteristic of this process, very high degrees of utilisation of the absorbent. In addition to the savings in the consumption of fresh absorbent the production of residues also is minimized.

Only a small fraction of the residues collected by the filter is pneumatically conveyed into the residue silo. The final product can be stabilized but also can be used without any further treatment for filling purposes in coal mines or as make-up material for the building material or cement industries.

The fresh absorbent is commercially available hydrated lime $\text{Ca}(\text{OH})_2$. For saving operating costs it can be produced locally in a dry slaking plant on the basis of burnt lime CaO .

The input of absorbent from the silo into the turboreactor is made by means of a controlled discharging device and a pneumatic conveying unit.

An economically very interesting alternative is the injection of comparably cheap limestone powder into the boiler, thus pre-desulfurizing the flue gases. Then the resulting product of fly ashes and product (CaO/CaSO_4) is used further in the Turbosorp® process without pre-dusting. The injection of limestone into the combustion chamber is known as "Furnance Limestone Injection" process on which comprehensive know-how is available from AE Energietechnik and Verbundplan.

The water which is required is pumped into a ringmain by means of a high pressure (HP) pump and injected into the turboreactor via a HP backflow nozzle. The effects of this process step consist in the cooling of the flue gas, thus increasing the relative humidity, and in moistening the great amounts of solids in the reactor, thus increasing the reactivity.

3.1.2. Main advantages of Turbosorp® process

- Low investment cost
- High removal efficiencies

SO ₂	<	95 %
HCl	>	98 %
HF	>	99 %
SO ₃	>	99 %
Dust	>	99 %
- High availability
- Short implementation times
- Low space requirements
- Final product marketable or suited for landfills
- Process without the production of waste water
- Optimum utilization of the absorbent due to repeated circulation of the solids
- Low operating cost due to savings in the absorbent
- Low maintenance cost due to the absence of moving parts in the reactor

3.1.3. References

Zeltweg (Austria)

Boiler: 137 MWel hard coal fired boiler

Flue gas capacity: 600,000 Nm³/h wet
SO₂ concentration: 2300 mg/Nm³ dry
SO₂ separation: > 91%
Product: stabilized product for landfills
Year of start-up: 1994

St. Andrä (Austria)

Boiler: 110 MWel hard coal fired boiler
Flue gas capacity: 450,000 Nm³/h wet
SO₂ concentration: 2500 mg/Nm³ dry
SO₂ separation: > 92%
Product: stabilized product for landfills
Year of start-up: 1994

Strakonice

(Czech Republic)

Boilers: 3 lignite fired boilers
Flue gas capacity: 310,000 Nm³/h wet
SO₂ concentration: 4200 mg/Nm³ dry
SO₂ separation: > 85%
Product: for landfills
Year of start-up: 1998

In the nearest future the first FGD in Poland based on Turbosorp® process will be constructed in a Group of Warsaw Co-generation Plants.

3.2 Desulfurization of flue gases in mechanical absorber – FHW technology

Another technology designed for smaller power stations (for gas flow rates lower than 400 000 Ncum/h), uses also dry absorbent in form of CaO or Ca(OH)₂ powder. The name FHW derives from first letters of the names of its creators (Friedl, Hein, Weichs). Desulfurization proceeds with high efficiency >90%, in the range of relatively high temperatures of gases – what makes outflow of gases to stack without reheating possible.

Desulfurization product obtained in the form of dry powder consists mainly of gypsum (60%), which is neutral for environment. Calcium sulfite content does not exceed 3% - what is an important advantage of FHW technology over other known devoid of wastewater desulfurization technologies.

3.2.1. Process principle

Likewise in Turbosorp® technology but as opposed to other semidry technologies a characteristic feature of this process is adequately controlled moistening of sorbent which at water content 8-12mass% preserves the properties of dry powder. Tiny water drops reaching sorbent particles enable dissolution of SO₂ and its binding with dissolved Ca(OH)₂, as it was described already in Turbosorp® process presentation. In the same time water evaporates into gas phase, what keeps temperature of particle surface close to the temperature of adiabatic gas saturation. Calcium sulfite formed in the first step undergoes oxidation to sulfate as a result of contact with oxygen contained in gas during long residence time of particles circulating in reactor.

Adequate cooling of flue gases to the temp. of 130°C before reactor may be reached with the use of specially constructed shell and tube heat exchanger (with vertical tube sections). It enables the use of waste heat of gases to reheating of water. Keeping the velocity of gases constant in the pipes, despite of actual installation load is a special feature of this construction. Waste heat recovery cuts fuel consumption substantially.

Flue gases are then intensely mixed with moistened sorbent while flowing cocurrently through a reactor. Before entering stack gases are thoroughly dedusted in an appropriate filter. Over 99% of solids contained in the system is circulated. All the time a small amount of product is withdrawn, and fresh hydrated lime is added continuously.

High temperature of the process (several degrees higher than dew point temperature of gas), also help in quick and complete drying of solids during their flow in the reactor turbulent zone. It preserves maintaining the filtration cloth dry even in cases of unexpected changes of gas parameters.

Due to two solutions of reactor itself there are two different schemes of FHW technology offered. Scheme of installation with vertical reactor is shown in fig. 2.

Fig.2. Scheme of desulfurization installation according to FHW technology with vertical reactor.

Main elements of DeSO_x installation presented correspond to solution of installation used in TKW in Kaiserslautern. These are:

- Shell and tube heat exchanger gas-water,
- Mechanical reactor with discharge, recirculation and dosing systems,
- Process water tank with refilling and atomizing systems
- Bag filter with self cleaning system
- Sorbent container (pressurized)
- Product container (pressure less) with aeration and desulfurization product discharge systems

Mixture of circulating product with some amount of fresh Ca(OH)₂ added is moistened in two-shaft screw mixer and introduced to the reactor from the top.

It comes into contact with flue gases flowing cocurrently while intensely mixed by chains rotating together with horizontally situated shafts mounted in pairs on 3 or 4 levels in the height of reactor. At the bottom of reactor solids settle mostly (ca. 80%). Particles entrained with gases flow to bag filter where are separated. Quadrilateral reactor having flat bottom and also flat-bottomed filter are connected with a wide steep channel. Gases are flowing through it to the filter, while dust separated there is removed by chain conveyor from beneath of the bags and slips down back to reactor. Another scraping mechanism situated at reactor's bottom collects dust at transverse channel. From this channel it is transported with screw conveyor through fresh lime adding feeder to bucket conveyor feeding a mixer placed at the top of the reactor. As it is seen from description the bag filter housing is not typical whereas inside it is a typical bag filter arranged in rows with sections and fully automated cleaned system with pulses of compressed air. Dedusted and desulfurized flue gases are directed to stack.

In a second type of FHW installation reactor is arranged horizontally. Its mixing devices are placed one after another at the same level in the bottom compartment that forms a base for a filter placed above within a two floor housing. This compact construction shown in fig.3 does not take much space.

Fig.3. Scheme of desulfurization installation according to FHW technology with horizontal reactor.

Flue gases adequately divided enter the reactor on the whole width of its front wall and flowing through the turbulent zone of rotating chains follow the draught induced path along

consecutive mixers before reaching the other end of reactor. There the stream changes its direction to vertical and enters the flow stabilizing chamber of the filter. Most of the dust particles settle, the rest falls down as collected on filtration devices during cleaning process. Scraped conveyor situated at chamber bottom shifts the powder to a transversal channel from which evenly distributed it falls down into a mixer installed along a gas inlet in form of a slit of similar length. In the mixer fresh hydrated lime is added and mixed absorbent is moistened with water atomized by many nozzles. Gas introduced through a slit entrains already prepared powder into reactor.

Chain mixers are arranged one after another. They are composed with shafts provided with bearings and electrical motors individually regulated. Chains attached to shafts periphery on hooks along a spiral line have length almost equal to shafts clearance to the reactor bottom and to the neighbouring shaft space of mixing. Automatically regulated parameters: sense of rotation and rotation speed of mixers enable change of residence time of both phases in wide ranges and their adaptation to actual needs.

Reactor, filter and other equipment may be made of carbon steel. Mixer parts: chains and their hooks attached to shaft should be made of manganese steel specially treated (tempered?).

3.2.2. Area of application and utilization of gas cleaning by-product

FHW method enables almost 100% removal of acid gases contamination of flue gases such as HCl, HF, SO₂, through their reactions with lime at gases temperatures 30 – 40 °C higher than dew point temperature for combustion of fuels containing less than 3% of sulfur. Average suspension density in the process may be even 200 times higher than in known processes of „dry sorption” or „dry scrubbing”. Perfect mixing of two phases in reactor enables not only absorption of acid gases but also adsorption of organic compounds such as dioxins and furanes , among other pollutants. In many cases of waste materials combustion, contaminated with organic compounds it is enough to hold the adequate cleanness of gases after the process (< 0.1 ng/Nm³).

In hazardous cases connected with nonuniform fuel composition there are used sorbent mixtures containing few percent of active carbon eg. Sorbalit, Dioxorber etc. It is then certainty of controlling of summed content of dioxines and furanes below the allowed limit of 0.1 ng/Nm³. Addition of activated carbon or coke makes adsorption of mercury and other partially volatile metals as thallium and lead possible.

In order that high degree of heavy metals separation should be reached, especially mercury, whereas sorbent does not contain activated carbon, enrichment of absorbent with adequate sulfur compounds is requisite. The two approaches lead to save running of installation and maintaining heavy metal concentrations in clean gas below the limits of their emissions. Offered FHW DeSO_x technology gives dry solid wastes that consist mainly of calcium sulfate (over 60%), small portion of sulfite (1-3%), calcium carbonate and fly ash. Such composition makes possible its treating as save deposit or as a material for further usage. Among possible ways of these wastes treating are:

- disposal (on open air or underground),
- usage as additive to aggregates and bituminous concrete in cement industry,
- in mortar production
- in road building
- as an additive in wastes cementing

The choice of a particular way of utilization should be preceded by economical analysis.

3.2.3. Main advantages of FHW technology

Direct moistening of sorbent before its contact with fue gases is an element of few other novel desulfurization technologies. In FHW method there are two other important factors added: high flow rate of recirculated sorbent and its intensive mechanical mixing with gases in reactor. Compact combination of reactor with dust filter in vertical or horizontal arrangement secures effective cleaning and dedusting of gases. Mechanical agitation creates also internal recirculation of sorbent that makes the path of solid particles in the reactor much longer in their flow through to the filter. In the turbulent zone sorbent particles crash and are subject to attrition and comminution. It helps in reaching of very high degree of sorbent utilization in the process. The effect of mechanical mixing is very efficient gas cleaning (at very low excess of Ca/S ratio), and generally acceleration of mass transfer processes eg. water evaporation rate. Owing to good drying of powder leaving reactor there is no problem with filtrating cloth durability due to its slow getting stuck and covered with deposits.

Therefore FHW method eliminates known technical problems that occur even in the case of novel, waste waters free absorption processes, and enhances efficiency of gases cleaning (with reference to SO₂ it is from 80 to almost 100%).

An important advantage of the technology is possibility of adjustment of installation parameters to:

- actual gas phase load
- SO₂ concentration in gas
- gas temperature at reactor inlet

through regulation of:

- circulating stream of sorbent
- amount of fresh Ca(OH)₂ added
- amount of water atomized on sorbent surface.

These parameters may be set independently what enables reaching very high installation flexibility i.e. running with high efficiency in the wide range of loads and conditions.

Worth mentioning advantages of FHW method are:

- wide range of gas cleaning applications – from power stations (< 150kW), chemical factories, brick-kilns to incinerators of hazardous wastes,
- high cleaning efficiencies reaching 99% in case of SO₂, HCl, HF and dust,
- possibility of method adoption to removal of dioxins, furanes and heavy metals from gases,
- oxidation of unwanted sulfite to chemically stable calcium sulfate due to high residence time of solids in the reaction zone,
- simple and efficient process of high technological and work safety,
- gas cleaning system totally independent from furnace during installation starts and stops, as well as easy adaptation to boiler load changes,
- start and stop without any problems with condensation in reactor or bag filter
- lack of deposits of sorbent on walls and corrosion
- low pressure drops (1- 3 mbar in reactor),
- low capital costs due to compact construction and possibility of use of carbon steel
- low space demand in buildings and easy maintenance by few employees,
- high effectiveness, due to possible heat recovery without preliminary dedusting and reheating of gases at the end,
- high availability (>98%)
- lack of visible stack plumes.
-

3.2.4. References of FHW technology

- a) desulfurization of gases in power stations or heat generating plants having coal fired boilers.

Both types of apparatus are installed in TKW in Kaiserslautern. Installation with vertical reactor is in constant exploitation for four years (15000h). All guarantees are fulfilled by FHW. Installation with horizontal reactor was commissioned at the end of the year 1999.

1) TWK, Kaiserslautern (Germany) with vertical reactor

Boiler 26 MWth, bituminous coal

Stream of gases 46 500 Nm³/h

SO₂ concentration 1000 mg SO₂/Nm³

SO₂ emission reduction >90%

Desulfurization product to deposit

Year of commissioning 1996

2) TWK, Kaiserslautern (Germany) with horizontal reactor

Boiler 14 MWth, bituminous coal

Stream of gases 23 000 Nm³/h

SO₂ concentration 1000 mg SO₂/Nm³

SO₂ emission reduction >90%

Desulfurization product to deposit

Year of commissioning 1999

b) Cleaning of flue gases from hazardous wastes incinerators.

Two lines of FHW installation with vertical reactor are in use to gas cleaning in Meuselwitz (Germany), since December 1998. Contaminated wood with 50% addition of chemicals is used as a fuel. After necessary load tests the fraction of chemicals may grow. Installation was designed for maximum concentrations of HCl and SO₂ not higher than:

2500mg HCl/ Nm³ and 1500 mgSO₂/ Nm³

Gas cleaning installation should fulfil 17 BImSchV regulation at any fuel composition.

3) Meuselwitz (Germany) with vertical reactor

Boiler 12 MWth, bituminous coal

Stream of gases 30 Nm³/h

SO₂ concentration 800 mg SO₂/Nm³

SO₂ emission reduction >90%

Desulfurization product to deposit

Year of commissioning 1998

4. Comparison of Turbosorp® and FHW technologies

Direct comparison of described technologies offered by BBP Environment was impossible as the sizes of working installation and process conditions are different. An attempt of making approximate evaluation of process parameters was made by design engineers from AE responsible for Turbosorp®, after their observation of FHW installations and making some measurements in TWK Kaiserslautern.

Processes were compared for a chosen gas flow rate 100 000 Nm³/h and conclusions formulated separately for both forms of FHW technology and Turbosorp®.

Turbosorp® technology compared with FHW (vertical reactor) shows:

- similar desulfurization efficiency at the same Ca/S ratio
- similar temperature conditions of desulfurization
- similar quality of desulfurization product,
- slightly higher electric energy demand (Turbosorp® 2,04 kW/1000Nm³
- FHW with vertical abs. 1.44 kW/1000 Nm³)

FHW (horizontal reactor) compared with Turbosorp® technology receives far better valuation:

- desulfurization efficiency at the same Ca/S ratio and the same temperature of gases is clearly better (as effect of better use of particles moisturing in perfect contact conditions of both phases due to intense mechanical mixing in reactor),
- desulfurization product contains more calcium sulfate and only traces of sulfite (effect of high temperature of process at which oxidation is faster),
- at the same process temperature predicted efficiency of FHW with horizontal reactor, as compared with Turbosorp® may be reached at much lower excess of sorbent (for temp. difference 25°C similar efficiency may be reached with Ca/S =1.3 for Turbosorp®, and Ca/F=1.05 in case of FHW),
- electrical energy demand for own purposes is approximately equal
(Turbosorp® 1.94kW installed for1000 Nm³/h,
FHW 2.00kW installed for 1000Nm³/h.

Two compared technologies are technically mature and checked in exploitation in Austria, Czech Republic and Germany. They are offered and build as „trunk key” installations of high desulfurization efficiency being to much extent independent of boiler load and conditions of combustion process.

Several years' service of FHW installations in Kaiserslautern under constant observation of their designers gave evidence of their reliability, low exploitation costs and lack of corrosion inside and on the outer surface of apparatus and piping in reactor building.

Waste heat recovery cuts fuel consumption substantially.

Having many advantages and as made of carbon steel and compact FHW installations supersede in Germany similar in principle but less effective and troublesome in practice processes eg. NID (known also in Poland –El. Łaziska).

Turbosorp® offered for power stations of higher capacity is to be build in EC Siekierki – Warsaw, Poland.

Presented offer of Babcock Borsig Power Environment may be realized with much contribution to a common enterprise of Polish firms. Activities of Babcock Steinmuller Wrocław Sp. z o.o. are directed to broad dissemination of information about DeSOx technologies and cooperation with Orderers to ensure the best choice of available BBP technology carefully fitted to individual project conditions.