Dry Injection of Sodium Bicarbonate Based Sorbent in Flue Gas for Air Pollution Control

Abstract

SOLVAir® Solutions has been launched by Solvay, a market leader in sodium products.

SOLVAir® Solutions is a wide range of sodium bicarbonate based products, services, technologies and treatment systems for air emissions control and associated waste management that meet the demand of industrial activities like **waste to energy (WtE), industrial boilers, large combustion plants, sintering and non-ferrous metals production (copper, molybdenum etc.), mineral wool, cement and glass production,** etc.

Currently several hundreds of customers worldwide are using dry injection of Sodium bicarbonate based sorbents in flue gases to mitigate pollutants to the most stringent legal limits.

Dry injection of Sodium bicarbonate based sorbents in flue gases is an easy and a fast-to-implement technology **with advantageous investment costs** and additional benefits in **SOx (SO_2 + SO_3) and HCl mitigation.** The processes are fully compatible with the most efficient nitrogen oxides (NOx) mitigation technologies.

Dry injection of Sodium bicarbonate based sorbents in flue gases can be implemented as main flue gas cleaning step or as complementary solution for cases like very high pollutant peaks mitigation, HCl selectivity and/or boosting of wet scrubbers, etc.

Solvay offers for flue gas cleaning a wide range of sodium bicarbonate based sorbents:

- SOLVAIR® S300 – standard sodium bicarbonate sorbent which is coarse and needs to be milled at customer site
- SOLVAir® SB 0/3 and SOLVAIR® S350 – pre-milled sodium bicarbonate based sorbents

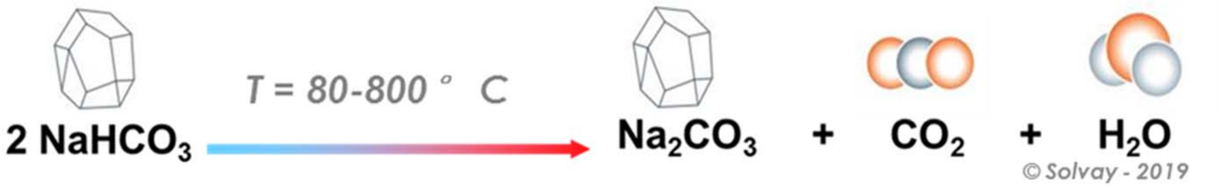
Achievable emission limits and mitigation performances both on an Electro filter and on a Bag filter:

- **HCl : 2 mg/Nm³ dry 11% O_2**
- **SO_2 : 2 mg/Nm³ dry 11% O_2 on a bag filter and 15 mg/Nm³ dry 6% O_2 on an electro filter**

Technical description

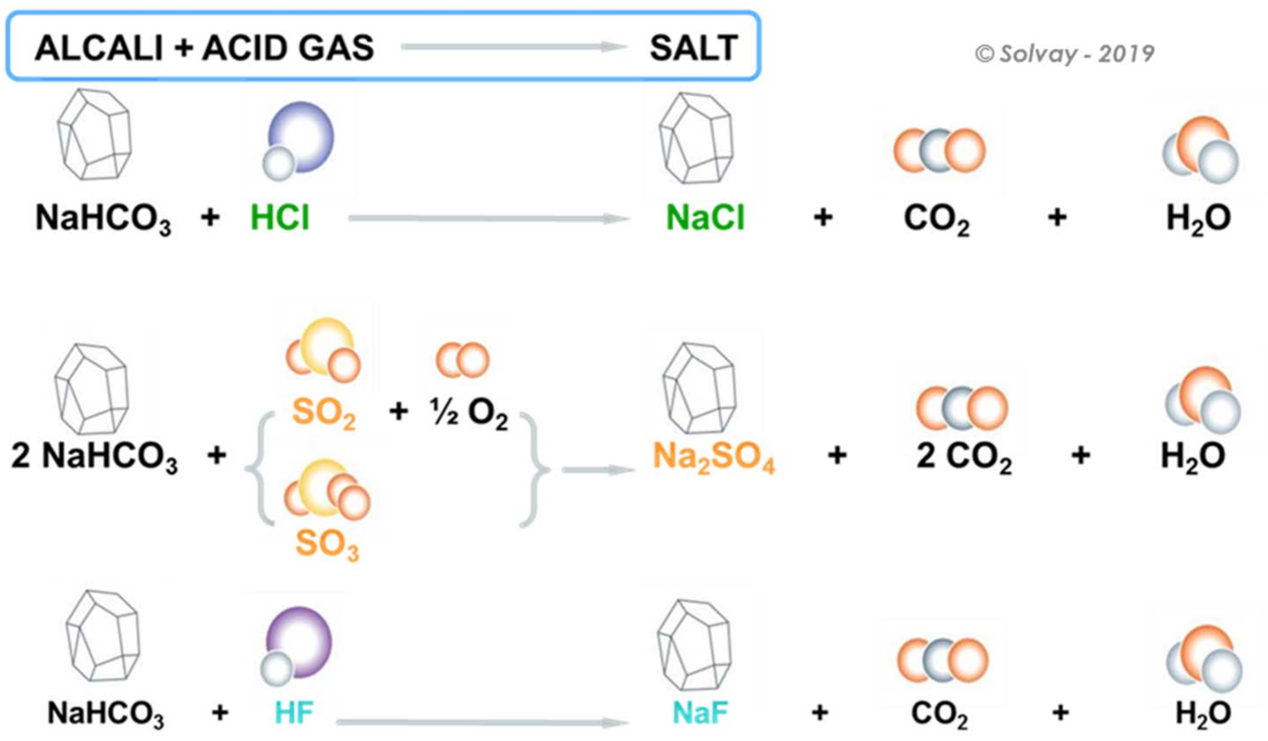
Working principle & chemical reactions

Sodium Bicarbonate ($NaHCO_3$) is well known for its buffering properties in chemistry. When exposed to the high temperatures of the flue gas, sodium bicarbonate ($NaHCO_3$) converts into a highly reactive sodium carbonate with a high specific surface (>10 m²/g) through the following reaction:

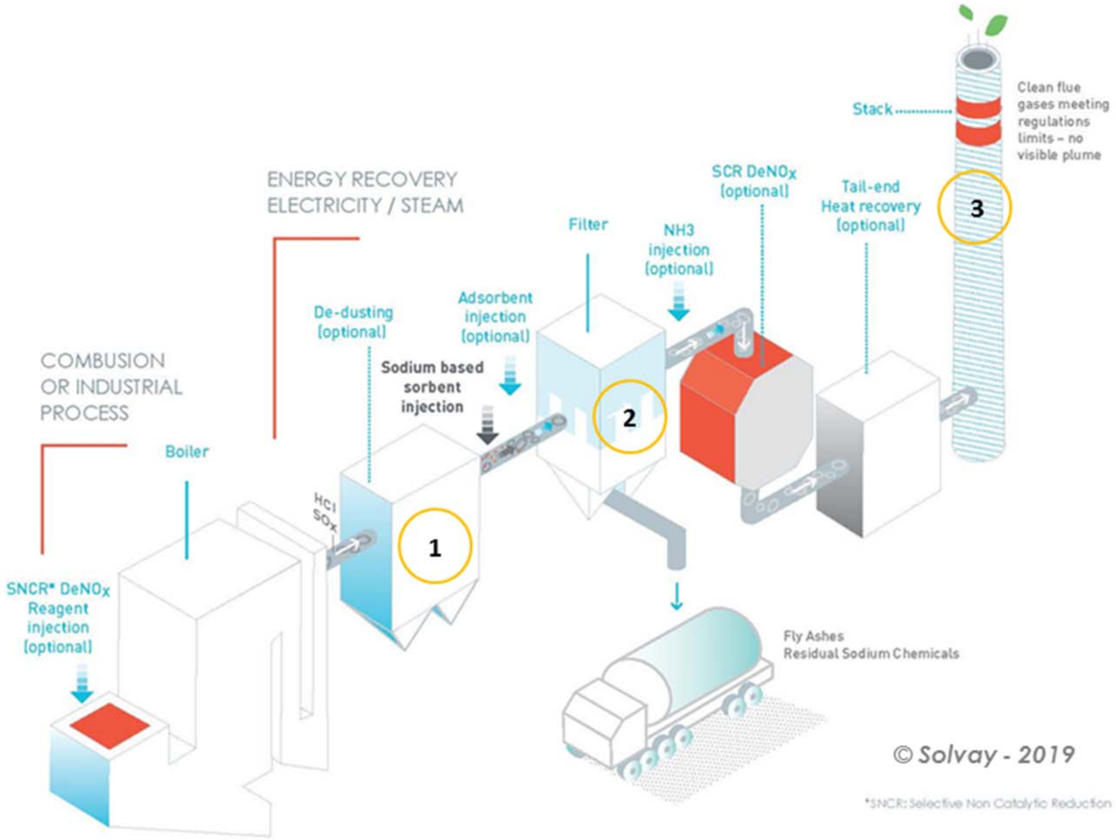


** Temperature always above due point*

This highly reactive sodium carbonate has a high affinity with different acid gases present in the flue gas duct and neutralizes them to form sodium salts, giving as net reactions:



Process description



1 - Storage, Dosing and Injection of sodium bicarbonate based sorbent in the flue gas

- Pre-milled sodium bicarbonate based sorbent is extracted from the silo with further direct injection into the flue gas duct where react with pollutants. (Optional: Coarse sodium bicarbonate based sorbent is extracted from the silo, milled finely and injected into the flue gas duct where react with pollutants.)
- Adsorbent injection for the complementary removal of heavy metals and other micro pollutants
- Lances can be used in order to improve the solid-gas mix, especially for plants with large ducts (cross section surface > $2m^2$)

2 - Reaction & Filtration, residuals storage

- Temperature has to be high enough to guarantee the thermal activation of the sorbent
- The required contact time is very short (2 sec), ducts are often long enough to guarantee that
- Use of an Electro static filter or a Bag filter
- The acids mitigation starts in the duct and continues inside the filter

3 - Stack

- Gaseous emissions are monitored at stack with the appropriate analytical systems
- The sorbent flow is controlled thanks to a feedback PID process control system on SO_2 / HCl measured at the stack to comply with the enforced emissions limits

The dry injection of sodium bicarbonate based sorbent has no effect on flue gas temperature (air intake is generally < 1% of the total gas flow).

Environmental performance and operational data examples

Dry sodium based sorbent injection has proved to be efficient at several hundreds of users in the world for more than 30 years.

Waste to energy

More than 300 incineration plants fuelled by municipal solid waste (MSW), Hazardous waste, RDF, Sewage sludge operate with sodium bicarbonate based sorbents. In general, HCl inlet varies from 800mg/Nm³ to 3000mg/Nm³ for raw gases to less than 5mg/Nm³ dry 11% O_2 at stack after dry bicarbonate injection in front of bag filters. HCl values at detection level can be reached (1-2 mg/Nm³), by increasing the sorbent injection. Depending on the design and level of optimisation, plants operate with the stoichiometric ratio down to ~1.

Operational data exemples

1 - Municipal solid waste (MSW) incineration:

Location	Incineration capacity, t/ year	HCl / SO_2 upstream, mg/Nm³ @ 11%O_2	HCl / SO_2 downstream, mg/Nm³ @ 11%O_2	$NaHCO_3$ consumption, t/year	In operation since, year
Belgium	63 000	1400-5000 / 300	10 / 50	1300	2004
Switzerland	33 681	500-2000 / 150-500	10 / 50	350	2015

2 - Sludge incineration at waste water treatment plants :

Location	SO_2 upstream, mg/Nm³ @ 11%O_2	SO2 downstream, mg/Nm³ @ 11%O_2	Sludge dry matter content, %	NaHCO3 consumption, kg/t sludge	In operation since, year
France	3000 – 5000 with peaks up to 9000	<50	27	18 (wet sludge)	2003
Poland	2800 (average)	<50	20	14-16 (wet sludge)	2017
France	800 with peaks up to 1300	40	100	40-50 (dry sludge)	2007

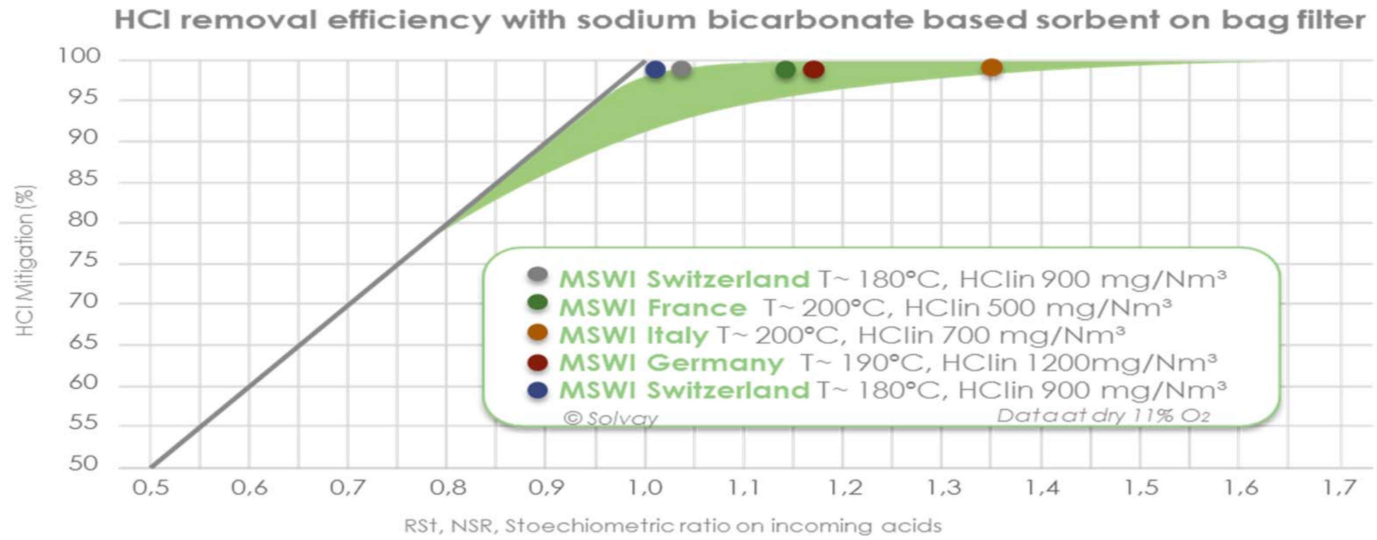
Operation performances based on the residue analysis in Energy from waste sector:

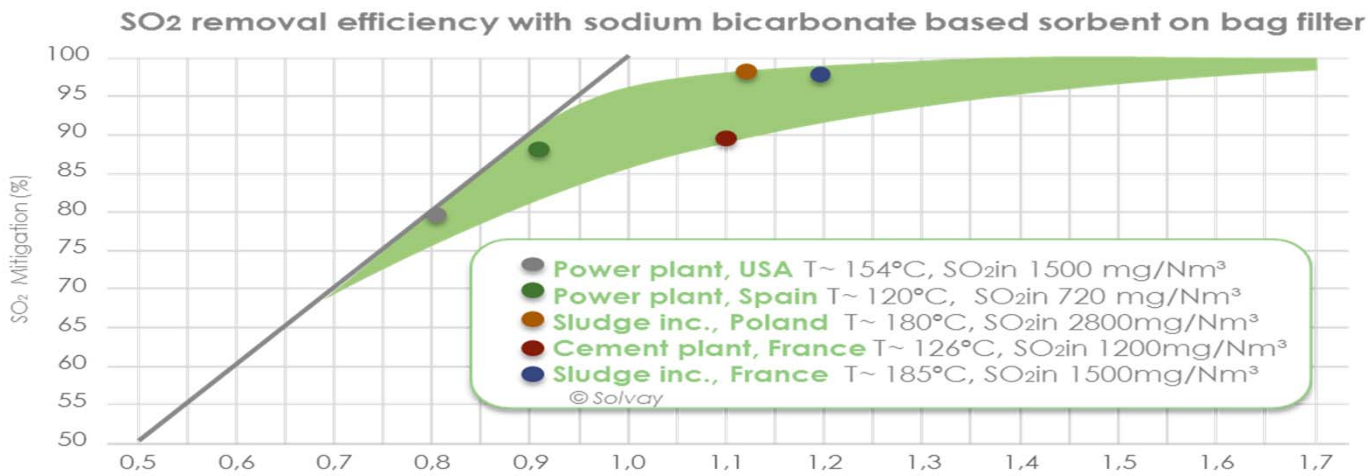
In order to evaluate the performances of sodium bicarbonate based flue gas cleanings, the stoichiometric factor (ratio) is considered. As the reaction is not complete, a light portion of sodium bicarbonate (in most cases 0 - 15 percent for waste to energy applications) will be activated but not neutralize acids and will be found back in residues mainly as sodium carbonate. It is calculated by dividing the injected sodium bicarbonate flow rate by sodium bicarbonate flow rate required in stoichiometric proportions to reach the performances of neutralization observed. This factor is generally given based on residue composition analysis. Operation performances based on the residue analysis are given in next table.

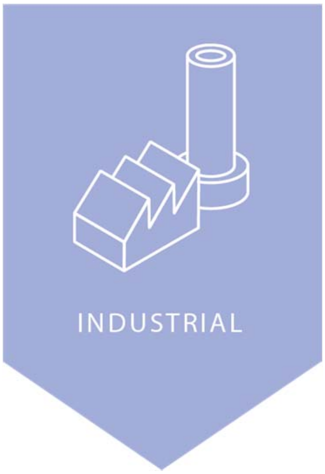
Plant location	Plant capacity, t waste/year	Waste type	Filtration type	Untreated gases Instant Min.-Max.		Clean gases Yearly avg.		SRa based on residue analysis
				HCl	SO_2	HCl	SO_2	
				mg/Nm³		mg/Nm³ dry		
Austria	146,00	Household construction	Bag filter	500-2,000	150-500	5	5	1.17
Belgium	65,000	Household	Bag filter	600-5,000	300-500	6	7	1.19
France	460,000	Household	Bag filter	500-1,000	80-300	5	5	1.15
Germany	552,000	RDF, Household	Bag filter + Recirc.	1,500-3,000	500-1,000	9	10	1.10
Italy	480,000	Household	ESP + Bag filter	400-1,000	50-300	2	<1	1.40
Luxemburg	174,000	Household	Bag filter	500-1,000	80-300	3	<1	1.13
Netherlands	384,000	Household Industrial	Bag filter	600-5,000	150-500	3	<1	1.06
Spain	360,000	Household	Bag filter	300-600	50-150	4	8	1.04
Switzerland	35,000	Household	ESP+Bag filter + Recirc.	500-2,000	150-500	2	13	1.00

Process performances observed on bag filter

"green zone" represents the potential optimization of sorbent performances depending on the configuration of the flue gas treatment system installed at user site







Industrial application

In the last years more and more customers of **various industry implement dry sodium bicarbonate based flue gas cleaning** to meet **IED (Industrial Emission Directive)** in EU and more **stringent regulations** in other countries

Stone wool producers mitigate the pollutions from the cupola furnace with sodium bicarbonate based sorbents. In general for the sector, the SOx emission decrease from 4000 mg/Nm³ to 1000mg/Nm³ dry 8% O_2, using bag or ceramic filters.

Since early 2000, 11 cement users world wide are using dry sodium bicarbonate base flue gas cleaning in order to eliminate pollutant from main flow. In general for the sector, the SOx emission decrease from 800 (peaks 1200 mg/Nm³) to less the 50mg/Nm³ dry 10% O_2, using bag filters.

Starting from mid - 2017 a **cement plant** operates with pre-milled sodium bicarbonate based sorbent to reduce the emission of HCl and SO_2 from the alkali by-pass. In order to be able to use waste as raw materials and as fuel during cement production, the alkali by-pass was installed at customer site to extract part of highly contaminated by HCl raw gases coming from the kiln. That allowed customer to maintain the homogeneous burning process without increasing the oxygen content. By using sodium bicarbonate based dry flue gas cleaning, HCl estimated emissions decreased from ~2900 mg/Nm³ to less than 10 mg/Nm³ dry 11% O_2, and SOx from ~125 mg/Nm³ to less than 20 mg/Nm³ dry 15% O_2 (in half hour average) on bag filter.

Starting form 2006, several **sintering productions** operate with sodium bicarbonate based sorbent. At sintering plant in Austria the emission has decreased from 700 mg/Nm³ dry 15% O_2 to less than 300 mg/Nm³ dry 15% O_2 thanks to dry sodium bicarbonate based sorbent injection before a bag filter. Due to flexibility of the dry sorbent process the stricter emissions limits can be achieved by increasing the flow rate of the sorbent.

Glass

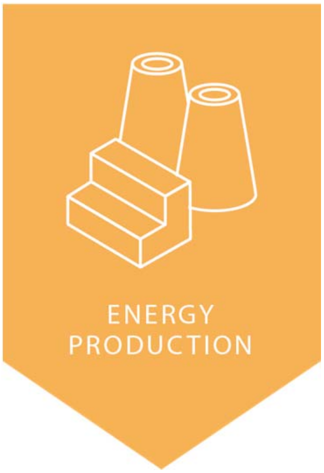
Since 2002, **19 glass users in Europe** implemented sodium bicarbonate based dry flue gas cleaning. Technology has proved its efficiency both in **float and container glass** production.

General operation conditions:

1. SOx inlet using natural gas as fuel:
   - float gals: 700 to 1000 mg/Nm³ 8% O_2
   - container glass: 1000 to 2000 mg/Nm³ 8% O_2
2. SO_3 inlet: between 7% and 20% of total SOx (expressed as SO_2)
3. Operation temperature at the entrance of the ESP: 250ºC - 400ºC, depending on the type / quality of the glass

Flue gas cleaning with sodium bicarbonate based sorbent has been implemented in order to comply with new emission limits and has demonstrated the following results:

- High reactivity towards SO_2 and SO_3 in combination with an ESP: up to 99% SO_3 and up to 98% SO_2 removal
- Stable operation of low temperature deNOx SCR (less then 350ºC)
- **100% residue recirculation as raw materials: sodium sulphate + soda ash**



Energy production

In **USA and further in Europe** start using sodium bicarbonate based dry flue gas cleaning technology for coal fired power plants with **various installed capacity from 50 MWth to 1300 MWe** to comply the legal limits.

Country	Capacity	SO_2 @ 6% O_2		Equipment	RS	FGT in operation
		Upstream	Downstream			
Spain	226 MWth	800-600	190	BF	0,8	2018
USA	2x660 MWe	1100	130	ESP	1,15	2014
USA	2x1300 MWe	650	140	ESP	1,4	2014

MWth - thermal generation capacity of power plant; MWe - electrical generation capacity of power plant

Starting from 2016, a mixed biomass and coal fired plant, in France, uses sodium bicarbonate based pre-milled sorbent. It's showing very good SO_x removal efficiency on a bag filter with a stoichiometric factor of one, starting from an upstream SO_2 level of 900 mg/Nm³ dry 6% O_2 and arriving below 200 mg/Nm³ dry 6% O_2 at stack.

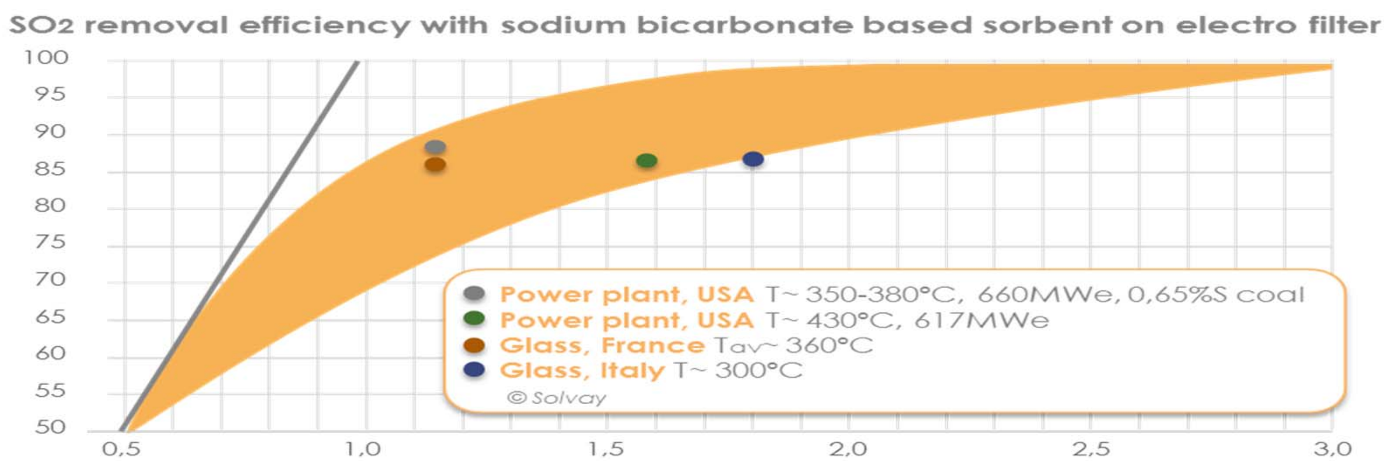
A power plant in Chile started operation in summer 2017 with pre-milled sodium bicarbonate based sorbent injected before a bag filter. Following new regulation, the SO_x emission limits decreased from 850 mg/Nm³ dry 6% O_2 to 250 mg/Nm³ dry 6% O_2 .

A fuel-fired district heating boiler operating in Paris, 180 MWth installed, uses sodium bicarbonate based sorbent with a bag filter to treat all the boilers (4 on fuel + 2 on gas). Achieved emission at stack is 165 mg/Nm³ dry 3% O_2 with removal efficiency 85% starting from an entry level of 1100mg/Nm³ dry. The sorbent flow is about 135 kg/h to treat the whole plant. Residues production ratio is 0,7 - 0,8 relative to sorbent injection flow, containing mainly sodium sulfate (80%) and sodium carbonate and bicarbonate (16%). These residues may be recycled thanks to the Resogypse® process.

An electrical company in Czech Republic is operating three coal-fired power plants with dry injection of sodium bicarbonate based sorbent before filter (ESP or BF). Following new regulation, the plants have been removing between 20% and 60% of the total SO_2 tonnage emitted per year (ex.: starting from 800mg/Nm³ dry 6% O_2 to 320 mg/Nm³ dry 6% O_2). The quantity of salts is very small compared to the total quantity of fly ashes (7-15%). The residues (salts and fly ashes) produced go to landfills.

Process performance observed on electro filter with temperature 250-400°C

"orange zone" represents the potential optimization of sorbent performances depending on the configuration of the flue gas treatment system installed at user site



Economics

Economics for each potential user of sodium bicarbonate based flue gas cleaning should be assessed based on its specific operation data. Below you may find several examples for various industry. CAPEX and OPEX costs are applicable to Europe. Outside of this geographical area the local cost should be taken into account

Total CAPEX

Coarse sodium bicarbonate based sorbent:
require grinder with approximate investment 30-300 kEuro/grinder (depending on size and geographical aria)

Pre-milled sodium bicarbonate based sorbent:
require handling and dosing equipment. Generally observed approach to use the silo that is already installed at customer site with further slight adaptation (if required) with CAPEX: from 0 to ~50kEuro/silo. In case the silo not available at customer site and should be newly build the cost will depend based on the geographical aria and could be estimated from 200kEuro to 300k/Euro per silo.

Total OPEX

Industrial sector	Plant capacity	Potential savings versus competing technology, kEuro/year
Energy from waste	160kt municipal waste/year	~250
Glass	700 t/day of float glass	~114

Conditions:

- Waste-to-energy: OPEX calculated based on used sorbent, residue production, water and heat used for plant that burn municipal waste. Limited changes in flue gas cleaning process were done. Further optimisation could lead to hire savings.
- Glass: OPEX calculated based on general glass recipe complying legal limit for standard size of flat glass oven according to BAT Reference Document for the Manufacture of Glass with 100% residue reuse.

Industrial sector	Plant capacity	Sulphur content in coal	OPEX, Euro/MW_{th}/0,1%S
Power generation	50 MW_{th} to 1300 MW_e	<1%	0,15 - 0,2

1USD = 0,91 EURO

Conditions:

- Quantity of used sodium bicarbonate based per-milled sorbent with indicative price in Europe/USA
- Quantity of fly ashes and residue produced with average treatment price in Europe/USA

Advantages of the technique

- The overall system does not require special monitoring, except some periodic maintenance (monthly when grinders are used).
- High flexibility to meet stricter limits: it is only necessary to increase the quantity of the sodium bicarbonate based sorbent that is injected in the raw gases.
- Dry injection of sodium bicarbonate based sorbent doesn't influence the particulate matter emission at stack.
- Sodium bicarbonate based sorbent is a safe product, no specific items regarding product safety.
- High energy efficiency : no decreasing of gas temperatures, limited number of equipment, energy recovery with heat exchanger
- No moisture: less corrosion than wet FGT, less maintenance, increased reliability

Technical considerations relevant to applicability

- All kinds of combustion processes: heavy oil, coal- fired (pulverized, grate) power stations, diesel engines, fluidized bed boilers, biomass, RDF, municipal solid waste (MSW) or industrial waste co-firing.
- Industrial processes: sintering and non-ferrous metals (copper, molybdenum etc.), mineral wool, cement and glass, etc.
- Filtration systems: Bag Filters (BF) and Electro Static Precipitators (ESP); Single filtration and Double Filtration; Main acids mitigation step and or pre-mitigation.

Driving forces for implementation

- more and more stringent regulation
- Flexibility to adapt to stringent limits
- no water need
- no need to release waste water to the environment
- lack of space to set up flue gas treatment
- urban encroachment asking for discreet plants: no plume at stack, limited footprint

Literature References

- Brochure SOLVAY S.A.: "more than 90% of SO2 removed" – 1990
- Bauer Th. - Thijssen M. : Neutrec® Trockenverfahren mit Natriumbikarbonat einschliesslich Aufbereitung und Verwertung der Reaktionsprodukte, VDI Seminar "BAT und preisorientierte Dioxin / Gesamtemissionsminimierunngstechnik, München 2000
- Höltje J. - Korte H-J. - NEUTREC - Verfahren zur trockenen Rauchgasreinigung für Abfallverbrennungsanlagen und andere industrielle Prozesse, VDI Bericht Nr 1241, 1996, 127 – 143
- Keener T.C., Davis W.T. - Study of the reaction of SO2 with NaHCO3 and Na2CO3, Journal of air pollution control Assiciation, Volume 34 (1984), 651-654
- Keener T.C., Khang S.J., Kinetics of the sodium bicarbonate-sulfuroxide reaction, Chemical Engineering Science, Vol. 48 (1993), 2859-2865
- Meijer E. - Reactiekinetiek van de gas-vast reactie van zwafeldioxide en natriumbicarbonaat - Diplomarbeit an der faculteit der werktuigbouwkunde, Universiteit Twente, 1996
- Morun B. - Trocken, halb trocken oder nass: Was ist wann sinnvoll - Betrachtungen zur Verfahrenauswahl aus der Sicht eines Anlagenbauers - No energy to waste Seminar 2007
- Siemens VAI Metals Technologies GmbH - Brochure Simetal MEROS(r) - 2010 / Website
- BREF Iron & Steel
- BREF Manufacture of Glass also for the recovery process in the emerging technology section
- BREF Waste Incineration
- BREF Common waste water and waste gas in chemical industry (CWW)
- J.P. Balland - Ready-to-use sodium bicarbonate in flue gas treatment – Waste Management, Volume 7, 2017)

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