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## CO<sub>2</sub> Capture and Re-use at a Waste Incinerator

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### Abstract

Twence is a waste processing and energy generation company located in the eastern part of the Netherlands. In the Twence plant waste is incinerated and in this process the waste is converted to valuable products like heat and power. In the flue gas produced from this Waste-To-Energy (WTE) plant a significant amount of CO<sub>2</sub> is released to the atmosphere. Recently a new innovative process developed by Procede Gas Treating B.V. has been commissioned at line 3 of the Twence plant. In this process CO<sub>2</sub> emitted to atmosphere, is scrubbed from the flue gas and this CO<sub>2</sub> is used for mineralization. The CO<sub>2</sub> is converted in an innovative new reactor configuration from sodium carbonate directly to sodium bicarbonate (SBC). The produced SBC slurry will directly be used at the WTE plant to purify the flue gas stream, before it is released to atmosphere. Due to the implementation of this process, which is unique in the world, the carbon footprint of the Twence installation is reduced. The new SBC plant produces 8,000 tons of sodium bicarbonate annually and to produce this amount of SBC 2,000 ton per year CO<sub>2</sub> is captured from the flue gas.

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## 1. Introduction

Recently a new innovative process developed by Procede Gas Treating B.V. has been commissioned at line 3 of the Twence plant, a Waste-To-Energy (WTE) plant located in the eastern part of the Netherlands. In this process the CO<sub>2</sub>, that usually is emitted to atmosphere, is in this new application, scrubbed from the flue gas and the obtained pure CO<sub>2</sub> stream is used to produce a sodium bicarbonate slurry (SBC). Instead of the conventional SBC flue gas scrubbing process, where dry SBC particles are used, this SBC slurry will be injected to remove the acid components from the flue gas, before the gas is emitted to atmosphere. Due to the implementation of this process the carbon footprint of the Twence installation is reduced. The new SBC plant produces 8,000 tons of sodium bicarbonate annually and to produce this amount of SBC 2,000 ton per year CO<sub>2</sub> is captured from the flue gas. This is approximately 2-3 % of the amount of CO<sub>2</sub> present in the flue gas and more than 90 % of this amount will be used to produce the bicarbonate. The CO<sub>2</sub> originates for about 50 % from biomass.

In this new process the captured CO<sub>2</sub> is used for mineralization and is converted in an innovative new reactor configuration from sodium carbonate to sodium bicarbonate (SBC). So instead of purchasing the expensive product sodium bicarbonate by Twence, the cheaper product sodium carbonate will be used as raw material in the new process. Another advantage of the new technology is, that 1 ton carbonate will be converted to 1.6 ton bicarbonate. This will result in additional cost savings due to lower transportation costs and related additional CO<sub>2</sub> emissions. The third and possibly most important advantage of this process is the negative carbon footprint. At the moment NaHCO<sub>3</sub> is mainly produced from Na<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub>, where the CO<sub>2</sub> is obtained by burning fossil fuels and a significant excess amount of CO<sub>2</sub> is required for this NaHCO<sub>3</sub> production. In this new process the Na<sub>2</sub>CO<sub>3</sub> is produced from “green” CO<sub>2</sub> produced at the waste incinerator and a closed CO<sub>2</sub> cycle is obtained at the site.

The sodium bicarbonate is used in the incinerator to remove impurities (acidic components) before the flue gas is emitted to atmosphere. The project was started on the 1st of July 2011 with the initial development of the new technology. The main objectives of the project were:

- Demonstration of an unique carbon dioxide capture technology leading to lower investment costs, lower consumption of absorption liquids, as well as lower operational costs;
- Demonstration of the re-use of the captured carbon dioxide for the on-site production of sodium bicarbonate to be used in the flue gasses cleaning system of the WTE plant;
- Evaluation of the concept of on-site production, storage and re-use of carbon dioxide;
- Review of the financial-economic perspective of the new technology.

With this process Twence is less dependent on the operational costs of the dry flue gas cleaning process, because the price of carbonate, the raw material of the new process, is much more stable than the price of bicarbonate. Based on a preparation of the business case, the payback period of the new process is estimated between 5 and 6 years depending of the assumptions used for the calculations. When these assumptions have been validated with plant data, a more detailed economic evaluation of the overall process will be presented.

End of 2014 the plant was commissioned at the Twence location in Hengelo, the Netherlands.

## Nomenclature

$a$	interfacial gas-liquid area [ $\text{m}^2 \cdot \text{m}^{-3}$ ]
$Al$	Hinterland ratio [-]
$C_{\text{CO}_2}$	$\text{CO}_2$ concentration in the liquid phase [ $\text{mol} \cdot \text{m}^{-3}$ ]
$D_A$	diffusion coefficient of component A [ $\text{m}^2 \cdot \text{s}^{-1}$ ]
$Ha$	Hatta number [-]
$k_L$	liquid side mass transfer coefficient [ $\text{m} \cdot \text{s}^{-1}$ ]
$k_{1,1}$	the reaction rate constant [ $\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ ]
$m_{\text{CO}_2}$	physical solubility of $\text{CO}_2$ in the solvent [-]
$r_{\text{CO}_2}$	$\text{CO}_2$ reaction rate [ $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ]
$\varepsilon_L$	liquid hold-up [-]

## 2. Validation of the new SBC injection technology

Before this project was implemented Twence used solid sodium bicarbonate particles and this solid material was sprayed in the flue gas channel. In the new technology a 40 wt.% bicarbonate slurry is produced and instead of SBC particles, this slurry is injected to remove the acidic impurities from the flue gas. The efficiency of this new spray technology with SBC slurry was tested at full scale (upto 1 ton/h slurry injection rate) at a Waste Power Plant in Bremen, Germany (BREWA). In figure 1 a summary of the test results are presented graphically. Initially the tests were started with the injection of dry SBC and slurry SBC, however, after some time the injection of dry SBC was stopped completely.

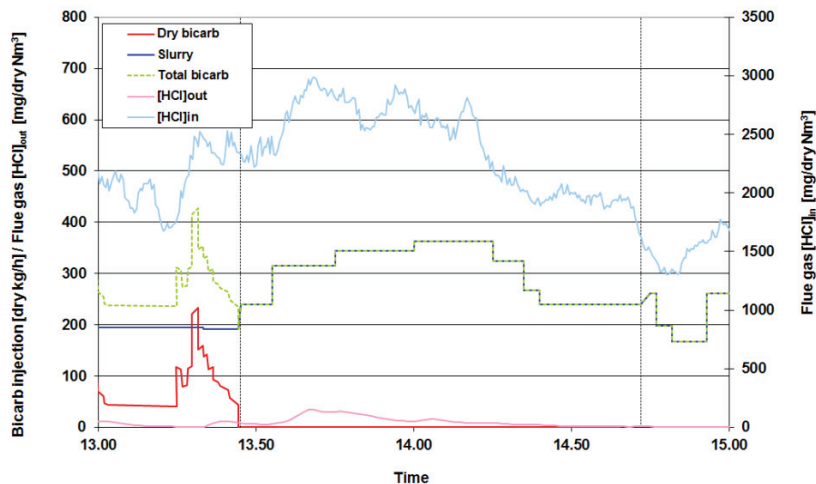


Fig. 1: Test results of SBC slurry injection at BREWA

From figure 1 can be concluded that also with the injection of SBC slurry, a high removal rate of acid components was achieved. In Figure 2 the amount of injected  $\text{NaHCO}_3$  is presented as function of amount removed acid gas.

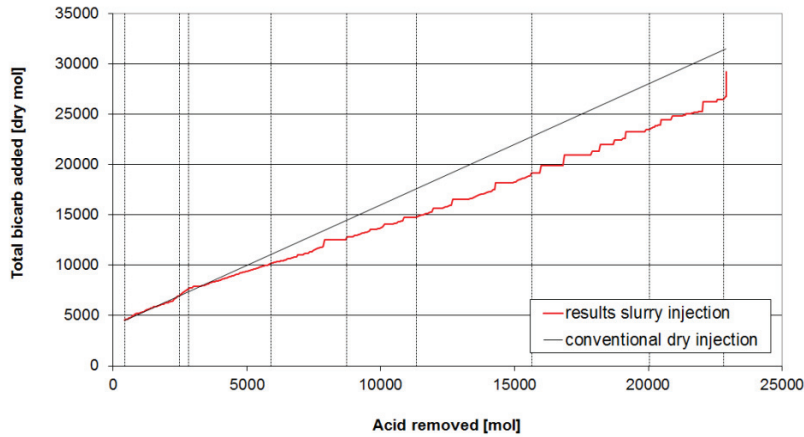


Fig. 2: Test results of SBC slurry injection at BREWA compared with dry injection performance; total amount  $\text{NaHCO}_3$  as function of total amount removed acid gas

From Figure 2 can be concluded that the efficiency of the SBC slurry (red line) is comparable and even slightly better than the efficiency of the conventional SBC injection technology (black line). Based on these tests results a design of a full size  $\text{CO}_2$  capture plant and SBC production plant was prepared for the “Line 3” at Twence. To develop this process from idea to commercial installation a strong consortium was formed between three companies:

- Procede was responsible for the R&D activities and developed the Conceptual and Basic Design of the plant;
- Bouman Process Technology was responsible for the Detailed Design, Equipment Selection and Supply, and the Construction Phase;
- Twence was responsible for the overall Project Management, Plant Integration and Commissioning Phase.

### 3. Process Design

Starting point of the project was to design and built a full scale SBC production plant to purify the total flue gas stream of line 3 at Twence. Therefore 2000 ton/year  $\text{CO}_2$  (= 250 kg/h) should be captured with a suitable  $\text{CO}_2$  capture process and with this captured  $\text{CO}_2$  8000 ton / year SBC will be produced. The SBC slurry will be produced from a saturated sodium carbonate solution resulting in a 40 wt.% SBC slurry. This high SBC concentration is required to minimize the temperature drop of the flue gas due to the slurry injection. The SBC production unit is designed to obtain a high conversion (> 90 %) of carbonate to bicarbonate at almost 100 % conversion of  $\text{CO}_2$ .

The production of SBC does take place according the following reaction equation:



The following process steps can be identified to produce the sodium bicarbonate from sodium carbonate:

- Soda Dissolve Unit;
- Quench and CO<sub>2</sub> Capture Plant;
- SBC Production Plant;
- SBC Injection.

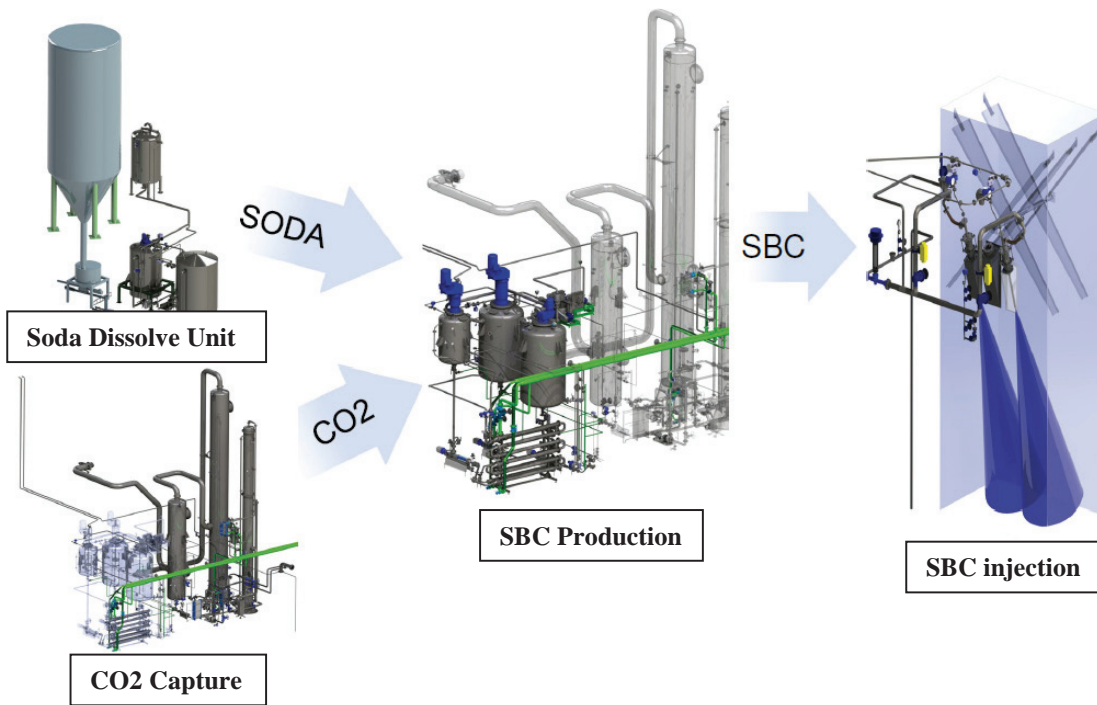
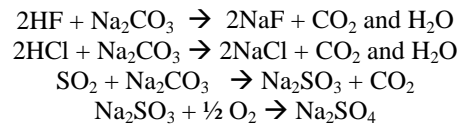


Fig. 3: Schematic overview of the SBC process installed at Twence

A side stream of the flue gas of “Line 3” is routed to a Quench. In this unit the flue gas is cooled and acidic impurities, which are still present in the flue gas in low concentrations, are removed. The pH of the quench liquid is kept constant by adding a small amount of concentrated sodium carbonate solution from the soda production unit. In the Soda Dissolve Unit solid soda is dissolved in water and this solution is routed to the bicarbonate production unit. The cleaned and cooled flue gas is routed to the CO<sub>2</sub> capture installation and in this installation pure CO<sub>2</sub> is produced with the solvent Bilisol<sup>®</sup>. This is a biodegradable solvent developed by Procede with a low degradation rate and very low volatility. The pure CO<sub>2</sub> is routed to two stirred tank reactors, which are connected in series. In two steps the sodium carbonate solution is converted with the CO<sub>2</sub> gas to a sodium bicarbonate slurry. This SBC slurry is buffered and pumped via a SBC circulation pipeline to two injection nozzles, where the slurry is injected in the flue gas channel together with steam. When the NaHCO<sub>3</sub> is contacted with the hot flue gases the NaHCO<sub>3</sub> is converted to Na<sub>2</sub>CO<sub>3</sub> according the following reaction equation:



Due to this chemical reaction and release of CO<sub>2</sub>, a Na<sub>2</sub>CO<sub>3</sub> particle with a large specific area is formed in the flue gas channel. The acidic impurities present in the flue gas are removed by chemical reactions with the produced Na<sub>2</sub>CO<sub>3</sub> particles. The following reactions do take place between Na<sub>2</sub>CO<sub>3</sub> and the impurities present in the flue gas:



For the operation of the CO<sub>2</sub> capture, bicarbonate production and injection process several utilities (steam, hot water and cooling water) are required. These utility streams have been derived from existing utility systems of Twence.

#### 4. Fundamentals of the SBC process

The gas treating part of the process (Quench and CO<sub>2</sub> capture plant) have been designed with the Procede Process Simulator. This is a rate based simulator specific developed for the development of gas treating processes [1]. All relevant properties of the Bilisol<sup>®</sup> solvent have been measured and incorporated in the process simulator. CO<sub>2</sub> reacts with Bilisol<sup>®</sup> according regenerative acid- base reactions in the liquid phase as commonly seen for amine scrubbing processes [2]. The regeneration of the solvent is carried out very efficiently in this process, because low grade heat is used from the WTE plant. The CO<sub>2</sub> capture plant built at Twence is a smaller version of the Bilisol<sup>®</sup> CO<sub>2</sub> capture plant operating in Delta (British Colombia) and also designed by Procede Gas Treating B.V. At this plant in Delta the CO<sub>2</sub> is captured from a flue gas stream coming from a wood burner and the CO<sub>2</sub> is directly used as fertilizer to growing fruits and vegetable. The capture of CO<sub>2</sub> from flue gas produced at a waste incinerator with Bilisol<sup>®</sup> has never been showed before. Performance data and solvent stability are not determined yet, and when these are available a more detailed overall performance of the Bilisol<sup>®</sup> technology can be determined.

The pure CO<sub>2</sub> stream from the desorber is routed to two NBC reactors were the following overall reaction takes place:



The overall reaction rate is determined by the CO<sub>2</sub> concentration (i.e. partial pressure) and OH<sup>-</sup> concentration (i.e. pH). The reaction rate of reaction 1 has been determined in literature. The reaction rate constant as determined by Pinsent et al [3] has been used to design the bicarbonate reactors. The absorption rate of CO<sub>2</sub> in soda has been determined experimentally in a lab scale stirred reactor and from these experiments it appeared that the experimentally determined absorption rate was 30-40 % higher than the absorption rate determined with the correlation of Pinsent [3], especially in the high CO<sub>2</sub> loading range (high conversion). Most likely explanation for this behavior is that CO<sub>2</sub> can also react directly to bicarbonate with carbonate in a similar mechanism as tertiary amines do react with CO<sub>2</sub> [4]. However, to develop a reliable, robust design, it was assumed that the absorption rate is determined by the reaction rate of CO<sub>2</sub> and OH<sup>-</sup> as is assumed in literature usually.

To determine the reaction regime, first the Hatta number was calculated. In this dimensionless parameter, the rate of reaction in the liquid film is compared to the rate of diffusion through this film. The Hatta number can be calculated as follows:

$$Ha = \frac{\sqrt{k_{1,1}C_{OH} - D_{CO_2}}}{k_L} \quad (2)$$

From this calculation it was estimated that the Hatta number was significant lower than 1 for chemical reaction 1. This means that the reaction rate is slow compared to the mass transfer. For this specific case the Hinterland ratio (Al) should be calculated, to determine the CO<sub>2</sub> concentration in the liquid bulk. The Hinterland ratio is defined as the ratio between the total reaction phase volume and the volume of the mass transfer film and can be estimated from the following correlation [5]:

$$Al = \frac{\varepsilon_L k_L}{a D_{CO_2}} \quad (3)$$

From the value of the Hinterland ratio it could be concluded that the concentration CO<sub>2</sub> in the liquid bulk was negligible, i.e. the reaction does take place mainly in the gas-liquid film. In this case the absorption rate of CO<sub>2</sub> in the reactor could be calculated with the following formula (no chemical enhancement):

$$-r_{CO_2} = m_{CO_2} k_L a C_{CO_2,G} \quad (4)$$

The physical solubility of CO<sub>2</sub> in the liquid ( $m_{CO_2}$ ) was derived from literature data and  $C_{CO_2,G}$  is determined by the CO<sub>2</sub> partial pressure in the reactors. The liquid side mass transfer coefficient ( $k_L$ ) and gas-liquid interfacial area ( $a$ ) are mainly determined by the reactor configuration and physical properties of the liquid phase.

Several reactor concepts have been evaluated and the two in series stirred reactor concept has been selected, due to high mass transfer rates, flexibility and robust design. In this reactor configuration two in series located stirred tank reactors are used. In literature several correlations are available to design stirred tank reactors. The first reactor is designed for approximately 70 % carbonate conversion, while the remaining conversion to bicarbonate is carried out in the second stirred reactor. Pure CO<sub>2</sub> is added to the reactors, no inert gas is available to produce interfacial area. For this reason the CO<sub>2</sub> is circulated over the reactor and part of the CO<sub>2</sub> is added into the slurry via a gas inducing impeller.

The 70 % conversion in the first reactor was based on the following two considerations:

- At conversions below 50 % undesired trona (Na<sub>2</sub>CO<sub>3</sub>·NaHCO<sub>3</sub>·2H<sub>2</sub>O) [6] may be formed and for this reason the conversion in the reactor should be significant higher to prevent the formation of this product (refer to figure 4 for the phase envelope of sodium carbonate-bicarbonate);
- At 70 % conversion the amount of particles is estimated at approximately 12 vol. % and above this solid concentration a steep decrease in mass transfer is observed in literature, i.e. [7]. At these conditions the mass transfer is difficult to predict and available correlations are less reliable.

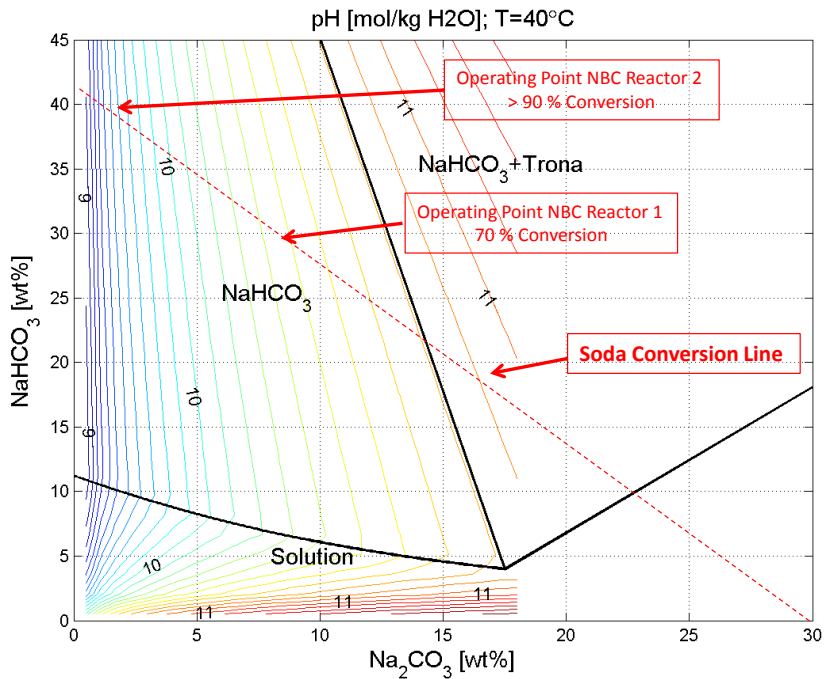


Fig. 4: Phase envelope of the sodium carbonate – bicarbonate system

So at 70 % conversion a relatively small reactor volume is required to produce the bicarbonate. However, at high conversions, the solid concentration increases to approximately 20 vol. % and at this solid concentration, the mass transfer is reduced significantly compared to the mass transfer in case no solids present in the liquid phase. So based on these assumptions and suitable mass transfer correlations from literature, the two SBC reactors have been designed.

In Figure 5 a picture of the total process CO<sub>2</sub> capture plant and SBC reactor system is presented together with a sample of the first produced SBC slurry.

At the moment the commissioning phase of the project is finished and the preparations have been started to go to continues operation. During this commissioning phase it was concluded that both the CO<sub>2</sub> capture plant and NBC production reactors were working according expectations. Full continues operation has been accomplished for several hours and the conversion from carbonate to bicarbonate is almost 100%. Slurry injection in the flue gas has been tested and was also successful.

During the commissioning phase some issues were encountered with the seals of the CO<sub>2</sub> compressor and also the formation of slurry in the head space encountered some unexpected problems, however, these have been solved now.

When the complete testing phase of the process has been finished, the plant will be handed over to the operation team of Twence for full continuously operation.





Fig. 5: (a) Overview of the SBC process installed at Twence; (b) picture of first produced NBC slurry

## 5. Conclusion

In this paper the development of a new process, which is the first in the world, has been described. The process is successfully developed from idea and lab scale tests to a full scale commercial process and has reduced the carbon footprint of the Twence plant. Also the overall, global carbon footprint is reduced, because for the conventional production of sodium bicarbonate more  $\text{CO}_2$  is used, by burning fossil fuels, than in the process described in this paper. The market for this process looks very promising. Twence is one of the 11 WTE plants located in the Netherlands. At a European scale at the moment circa 450 WTE plants are in operation. Nowadays, these plants heavily invest in sophisticated filtering devices to minimize the emissions to the atmosphere. Sodium bicarbonate has shown to be a very effective and efficient chemical for flue gas cleaning compared to other processes and an increasing amount of WTE plants recently switched to using this product or are considering switching. The installation described in this paper, which is unique in the world, may become an improved second generation bicarbonate flue gas cleaning process with a closed  $\text{CO}_2$  cycle with respect to the flue gas cleaning process.

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