BIOLOGICAL FLUE GAS DESULPHURISATION "BIO-FGD"

Introduction

Flue gases can be a major source of sulphur oxides [SO_x], nitrogen oxides [NO_x] and particulate emissions and most national and local environmental agencies are now implementing restrictions on the release of these pollutants to the atmosphere. Wet gas scrubbing with dilute sodium hydroxide or limestone solutions can remove both SO_x and particulates but both technique require the continuous addition of large volumes of neutralizing agent and the handling and disposal of similar volumes of effluent.

By combining two proven technologies, the CPT *Reverse Jet* scrubbing system and the *"Bio-FGD"* regeneration process, Clearwater is now able to offer a process that effectively treats flue gas with the production of minimum solid or liquid effluent.

Features of the Combined Technologies

The Reverse Jet scrubbing system is unique in its ability to perform multiple functions in a single vessel. Using a sodium bicarbonate solution as the scrubbing solution, these include:

- Quenching of hot flue gas
- Removal of particulates
- Efficient absorption of SO_x

Originally developed for use in the paper and cement industries, CPT's Reverse Jet scrubbing technology is ideally suited for long-term operation in the hot, abrasive environment of flue gas treating. The CPT Reverse Jet is not obligatory for the Bio-FGD system; other scrubber systems are also possible.

The sodium bisulphite/sodium sulphate solution formed in the Reverse Jet scrubber is filtered (when required) to remove solids and then routed to the anaerobic *"Bio-FGD"* bio-reactor where all sulphur species are converted to sodium bisulphide using hydrogen gas (or high COD wastewater). The sulphide is converted in a second (aerobic) *"Bio-FGD"* bioreactor into elemental sulphur.

"BIO-FGD"

Process Flow Scheme

The proposed system relies on the scrubbing of the flue gas to remove sulphur oxides and particulates followed by filtration and bio-regeneration of the scrubbing liquid. Particulates are recovered as the only solid waste. The sulphur is recovered as a hydrophilic 'bio-sulphur' from the second *"BIO-FGD"* bio-reactor. The flow scheme is represented in *Figure 1.*

Figure 1. **Scheme of the Flue Gas Treatment Process**

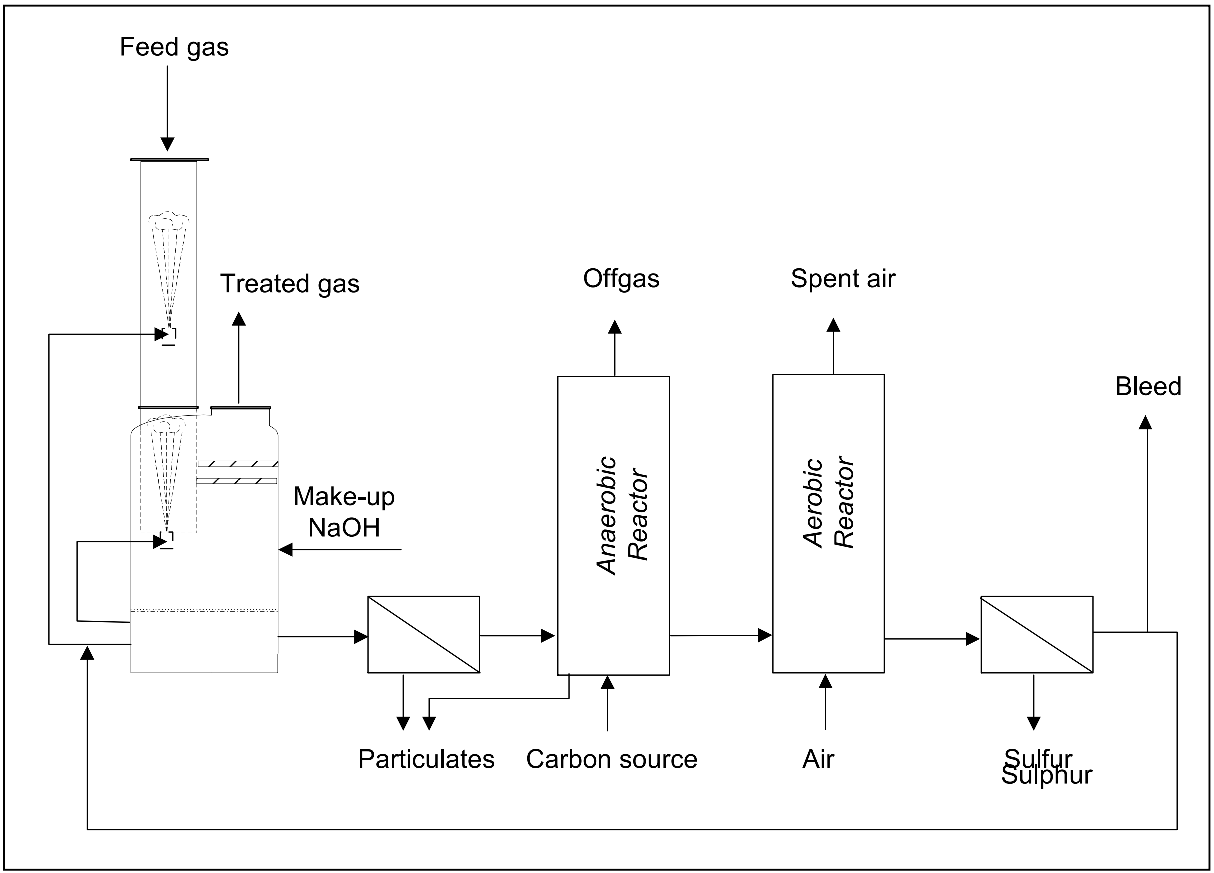

Figure 1 **Reverse Jet Scrubbing**

The first process step, the efficient transfer of sulphur oxides and particulates from the flue gas to a sodium phosphate buffer solution, is completed using the Reverse Jet gas scrubbing system. The heart of this system is the Reverse Jet, a large bore, open-throated nozzle that creates a zone of intense mixing in a vertical duct. Flue gas enters the top of the duct and collides with the scrubbing solution forced upwards through the nozzle. A standing wave of highly turbulent flow, *the Froth Zone*, is created where the up-flowing liquid from the jet is reversed by the hot, down-coming gas. The gas is quenched, the catalyst fines are removed and the SO_x [mainly SO_2 with some SO_3] is absorbed into the solution as sodium bisulphite [$NaHSO_3$] and sodium sulphate [Na_2SO_4].

$$SO_2 + NaHCO_3 \rightarrow NaHSO_3 + CO_2$$
$$SO_3 + 2\ NaHCO_3 \rightarrow Na_2SO_4 + 2\ CO_2 + H_2O$$

The products from the Froth Zone fall to the lower chamber of the Reverse Jet scrubber where the liquid separates and the cooled flue gas exits the system through a vane demister. Part of the scrubbing solution is recycled through the jet nozzles to remove more SO_x and particulates from the flue gas and part is routed to an optional filter (typicall rotary drum) to remove solids before being sent through an optional water cooler to the anaerobic *"Bio-FGD"* bio-reactor.

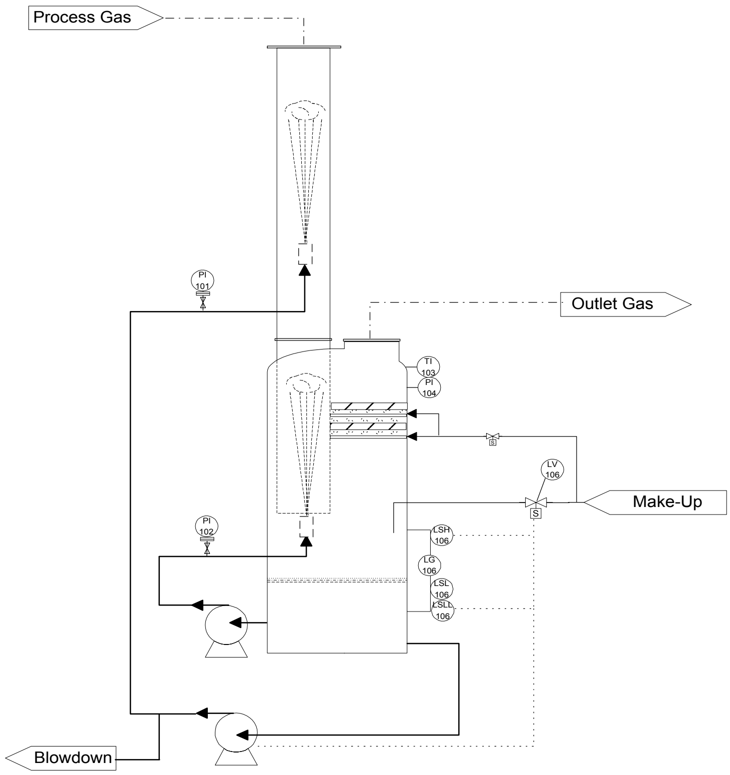

Figure 2 **Reverse Jet Scrubber**

The cooled flue gas will be saturated with water at the exit temperature and make-up water will need to be added to the system to compensate for water

evaporation in the scurbber and through the bleed. The bleed is required to discharge chloride that has been washed in.
Although the Reverse Jet system has several advantages, other scrubbing systems can be used without any problem.

Biological Regeneration

In the first (anaerobic) *"Bio-FGD"* bio-reactor, bisulphite and sulphate ion from the Reverse Jet scrubber are reduced anaerobically to dissolved sodium sulphide [NaHS] using naturally occurring, living micro-organisms. During the biological conversion electrons are consumed which can be provided by either hydrogen gas or a source of low grade COD (conversions below with hydrogen):

$$NaHSO_3 + 3\ H_2 \text{ -> } NaHS + 3\ H_2O$$
$$Na_2SO_4 + 4\ H_2 + NaHCO_3 \text{ -> } NaHS + 4\ H_2O + Na_2CO_3$$

The sulphide is transported dissolved as bisulphide to the second (aerobic) *"Bio-FGD"* bio-reactor where the bulk of sulphide is converted to elemental sulphur:

$$NaHS + 0.5\ O_2 \rightarrow NaOH + S^o$$

with a small part fully oxidized to sodium sulphate. The effluent from this reactor contains sulphur that is separated and further processed (i.g. dewatering). The regenerated liquid is returned to the Reverse Jet scrubber for further duty. Depending on the selected sulphur disposal option, the sulphur stream is either collected as a 10-20% sulphur slurry or as a 60-65% cake. Any dissolved sodium sulphate from the aerobic reactor returns with the regenerated buffer solution to the scrubber where it becomes a small part of the new bisulphite/sulphate load.

Both (anaerobic & aerobic) *"Bio-FGD"* processes are normally completed in 'gas lift reactors'. The gas-lift system is a proprietary design; the two designs are very similar and both operate on a continuous basis. The anaerobic reactor is shown below.

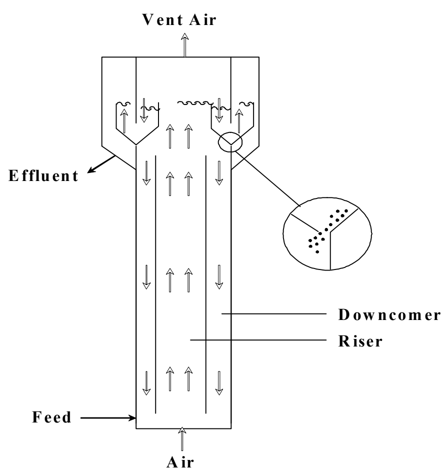

Figure 3. **The Aerobic Bio-reactor**

Both reactors are vertical vessels typically between 8 to 30 meters high depending on the required volume and fitted with an inner riser. The reaction gas [air or hydrogen] is passed up the inner riser to encourage good contact and circulation. The top of the reactor acts as a 3-phase separator where gas, treated liquid and bio-mass are separated. The reactors are designed as closed systems so any unwanted emissions to the atmosphere are eliminated.

Ambient operating conditions allow extensive use of non-corroding construction materials like GRP, polypropylene and polyethylene for piping, valves and other process equipment. These materials offer long life.

Start-up of any *"Bio-FGD"* unit is straightforward. After initial inoculation with suitable micro-organisms, the biomass grows and develops to reach design operating conditions normally within 1 week when using H_2 gas as electron donor and within approximately 1 month when using a small high COD waste water stream as carbon source. The system is robust and adaptive, quickly adjusting to the process demands and resilient to process changes or feed upsets. With little attention, the population will remain viable indefinitely because it is constantly renewing itself; replacement of the micro-organisms may never be required.

Like other processes, the key to successful operation is good process control and biological systems are no exception. Conductivity, temperature, pH and redox potential are continuously measured on-line and a process loop control system is used to maintain them within the desired range. On-line measurements are complemented by periodic laboratory analyses for sulphur species, nutrients and solids concentration. A small bleed stream is required to compensate for the nutrient supply, to remove reaction by-products and to bleed off washed in halogens chloride and fluoride.

Many years of commercial operating experience shows that both the aerobic and anaerobic *"Bio-FGD"* processes adapt readily to changes in feed sulphur levels. The population of micro-organisms is very robust and will recover quickly from process upsets.

Solids Handling and Sulphur Processing

The Reverse Jet scrubber can be designed to capture most of the particulates. The particulates are removed from the liquid stream before entering the first biological reactor by means of a conventional solid/liquid separation step. Both bioreactors are 'gas-lift loop' reactor type. They are especially designed for thorough mixing of gas and liquid containing high solids with concentrations up to 200 grams per litre. At the top of the anaerobic reactor a proprietary gas/liquid/solid separator is installed to retain the solids and prevent carryover to the second biological reactor. Particulates are removed from the reactor together with small amounts of excess biomass. One of the advantages of working in this sulphide-rich environment is that metals such as nickel and vanadium removed from the flue gas and dissolved in the scrubbing liquid are precipitated as metal sulphides and are removed with other particulates.

The elemental sulphur produced in the aerobic bioreactor, approximately 95% of the total sulphur load, is recovered from the aqueous stream as a slurry of typically 10-20% dry solids content in a separator. The sulphur purity is 95% or better, the remaining 5% is organic biomaterial and trace salts.

There are three options for handling this slurry:

1. It can be dewatered using a continuous decanter centrifuge resulting in a sulphur cake of 60 - 65% dry solids content. The water is returned to *"Bio-FGD"* as process make-up. The sulphur purity is ~ 95%. This sulphur cake can be safely land filled as non-hazardous waste or used locally as a fertiliser.

2. The decanter centrifuge step can be used with the addition of a water wash through the centrifuge followed by drying. This results in a sulphur product with 70% dry solids content and 99% sulphur purity. The wash water can be returned to *"Bio-FGD"* as process make-up water. This sulphur is suitable for addition to a refinery sulphur pit, for fertilizer manufacture or for use in sulphuric acid manufacture where such facilities exist.

3. The sulphur slurry can be directed to a sulphur smelter where molten sulphur of 99.8% purity is produced for sale. The water is returned to *"Bio-FGD"* as process makeup and the solid impurities, now representing less than 2% of the total sulphur can be land filled.

Treated Effluent Composition

Should it prove necessary to drain phosphate solution from the circuit, the treated effluent stream from the aerobic reactor will have a pH of approximately 8.5 to 9.0 and a temperature of 35- 55°C. This stream contains <1 ppm H_2S, and has a low BOD and COD and can be safely discharged in the wastewater treatment system.

***"Bio-FGD"* Operations**

Routine operator tasks include:

- Check operation of all pumps
- Check level of nutrient supply tanks
- Check for all flows
- Check process data; make adjustments if required
- Perform routine analytical tests

The *"Bio-FGD"* unit does not require regular shutdowns for overhaul. All routine maintenance can be performed while the unit is operating. Once the bioreactor is started up, no further handling of micro-organisms is required. The micro-organisms used in the bioreactor are naturally occurring and are harmless. No special precautions are required around the bioreactor beyond what would normally be appropriate for exposure to a sulphide-containing stream.

EXAMPLE OF BIO-FGD USED FOR IGCC "SYN-FUEL" PROCESS USING HIGH-SULPHUR PETROLEUM COKE AS FUEL

The gas composition for the calculation has been based on a 'Syn-Gas Co-generation Power Plant. In this flow table, the exhaust from the economiser has been used as the basis. The SO_2 and hydrogen chloride concentration have been summed. It has been assumed that dust is not present or not washed in at the stage of where SO_2 is removed.

This has resulted in the gas composition as basis for the data given in Table 1. All data has been converted to SI.

Table 1: Gas composition for the estimation of the required data in SI-units.

Component		unit	kg/h
Nitrogen	75.9	vol%	609742
Oxygen	2.9	vol%	26157
CO	0.00	vol%	0
CO_2	16.2	vol%	204471
H_2O	4.5	vol%	23327
CH_4	0.00	vol%	0
HCl	6.5	ppm	6.8
HF	0.00	ppm	0
SO_x	5016	ppm	9210
Total	100.00	vol%	872913

Based on the data in Table 1, the estimation of consumables given in Table 2 has been determined.

The acetic acid, urea and phosphoric acid are required as a nutrient. Instead of acetic acid, also a (waste) ethanol stream can be used. Phosphoric acid can also function as additional buffer, although as this stage that appears not to be required in this case.

Table 2: Estimated requirement of consumables

Component		unit
Hydrogen	14000	Nm3/h
Electricity	3	MW
Air	33000	Nm3/h
Caustic (50 wt%)	80	kg/h
Acetic acid (80% tech grade)	0.30	m3/h
Phosphoric acid (75 wt%)	10	kg/h
Urea	60	kg/h
Sulphur coagulant & flocculent to be determined during operation		

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Block schematic of a typical "Bio-FGD" installation

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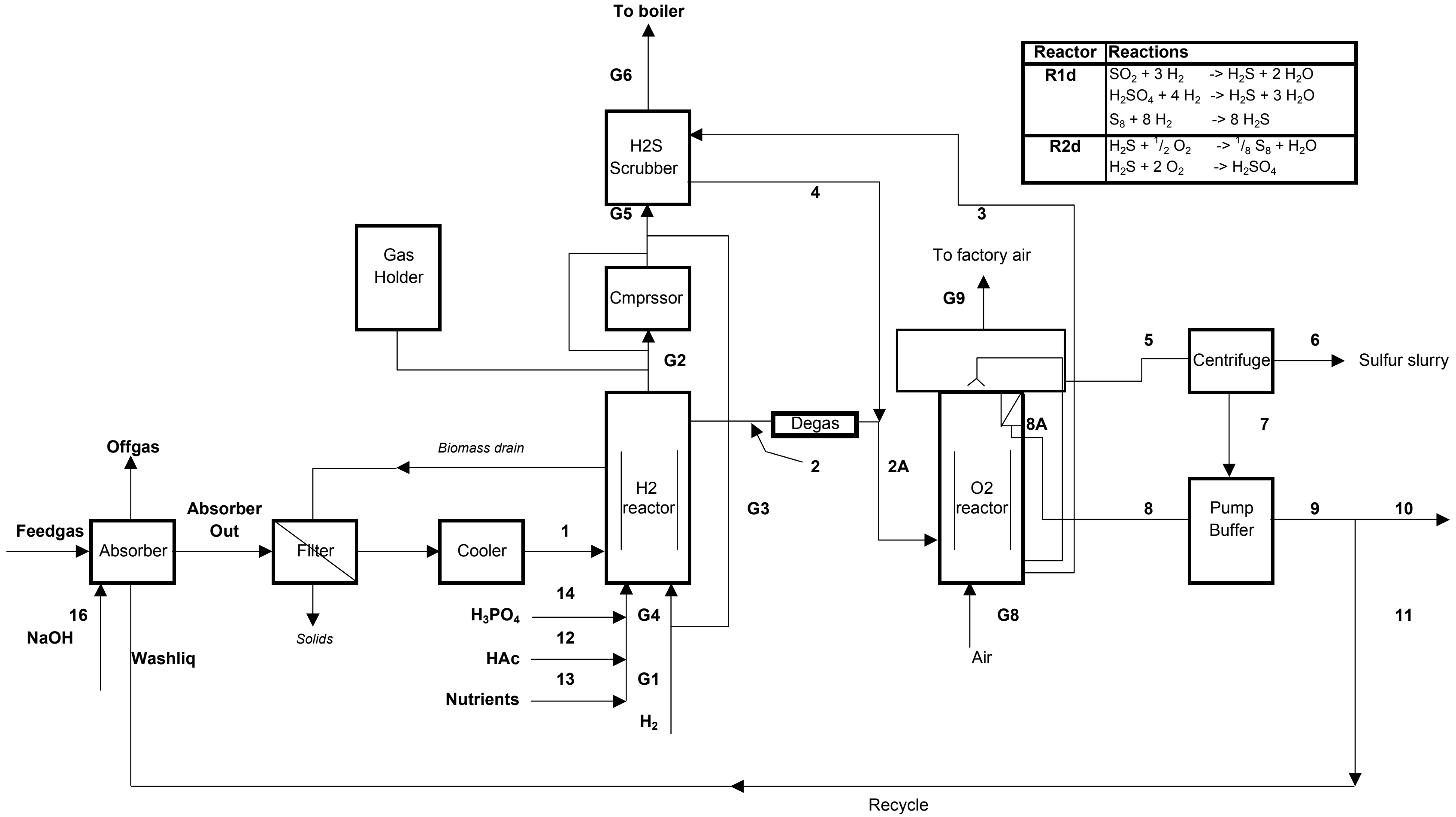
Block schematic of a typical "Bio-FGD" installation.



Reactor	Reactions
R1d	$SO_2 + 3\ H_2 \rightarrow H_2S + 2\ H_2O$
	$H_2SO_4 + 4\ H_2 \rightarrow H_2S + 3\ H_2O$
	$S_8 + 8\ H_2 \rightarrow 8\ H_2S$
R2d	$H_2S + {}^1/_2\ O_2 \rightarrow {}^1/_8\ S_8 + H_2O$
	$H_2S + 2\ O_2 \rightarrow H_2SO_4$