FLUE GAS FOR CARBONATATION

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Abstract

Flue gas is used for carbonatation in five refineries in southern Africa. The gas which contains about 12% CO_2 by volume is scrubbed to remove sulphur compounds and to cool the gas to about 50°C. Water scrubbing is sufficient for the gas from bagasse fired boilers but a second scrubbing with a 5% sodium carbonate solution is required if the boilers are oil or coal fired. The volume of flue gas required (at 50°C and 70 kPa) is about 140 m^3 per ton of solids in melt.

Introduction

Although no reference has been found on where and when flue gas was first used for carbonatation in sugar refining, the process appears to have been developed in Britain from where it spread to carbonatation refineries all over the world.

Before the advent of flue gas carbonatation, the carbon dioxide required for clarification was produced by burning limestone in kilns. This process is still used in beet juice clarification and in plantation white sugar production from cane in Taiwan. In South Africa, two back-end refineries (Gledhow and Pongola) still burn limestone for carbon dioxide production for refining. The use of liquid carbon dioxide has been investigated by a local back-end refinery but was found to be much more expensive than kiln gas.

There are few references on carbonatation using flue gas[1,2,3,4] and the scrubbing and compression of the gas are generally not described in any detail in the available literature.

The process is used in five refineries in southern Africa (Dwangwa, Hippo Valley, Ubombo Ranches, Malelane, and the Durban Tongaat-Hulett refinery) but the equipment and conditions vary within fairly wide limits. An attempt is made in this paper to define the operating conditions and the capacity of the equipment required to assist in the optimisation of flue gas carbonatation. Opinions expressed are not always substantiated by references and are often based on the author's evaluation of practices at various refineries and on unpublished studies and reports made available by the refineries.

Advantages and disadvantages

In comparison with lime kilns, the main advantages of flue gas carbonatation are:

(a) The lower capital cost due to elimination of the lime kiln and limestone handling equipment.

(b) The lower operating cost especially where limestone has to be transported over long distances as is the case in South Africa. Even after making allowance for the fact that the lime required for both the raw house and the refinery, plus an excess that can be sold, is a by-product of carbon dioxide production from limestone, the costs of materials were estimated to be in the ratio of 1,23 to 1 in favour of flue gas.

These advantages must be balanced against the following disadvantages:

(a) Additional scrubbing with sodium carbonate solution if sulphur-containing fuels are burnt.

(b) The lower carbon dioxide content of flue gas (about 12% by volume) compared to kiln gas (about 30%) which requires the compression and piping of a larger volume of gas.

Flue Gas Scrubbing

The composition of flue gas and the type of scrubbing required will depend on the type of fuel burnt. In the case of coal or oil, the flue gas will contain sulphur (mainly in the form of sulphur dioxide) which must be washed off before the flue gas can be used for carbonatation. If the flue gas is obtained from a bagasse fired boiler, it will have a low sulphur content and can be used after scrubbing with water only.

It is obviously advantageous to draw off the flue gas after any scrubber with which the boiler is equipped. If it is a wet scrubber, the gas will require little additional washing, but it is safer to have a separate water scrubber before the compressors. In the scrubbers the gas is washed with water which removes 99% of the fly ash and most of the sulphur in the case of bagasse fired boilers. With coal and oil fired boilers, the residual sulphur content of the flue gas after the first scrubbing may be high enough to warrant a second scrubbing[2] with 5% sodium carbonate solution. The sodium carbonate solution is normally recycled and Chapman (in Ref.[2]) quotes a consumption of 50 to 75 grams of soda ash per ton of sugar melted, while Hulett Refinery reports 13 to 16 grams. An analysis of SO_2 in flue gas carried out at this refinery showed an initial value of 400–500 ppm which was reduced to 0,5 ppm after the first (water) scrubbing and to less than 0,1 ppm after the sodium carbonate scrubbing.

The scrubbers should be designed for maximum contact between gas and water. There are a number of designs in which this requirement is met, and sketches of three types of scrubbers found in southern African refineries are shown in Figure 1. The first three operate on flue gas from bagasse fired boilers, while the fourth handles gas from a coal fired boiler and consists therefore of two stages (a) the water scrubber and (b) the sodium carbonate scrubber.

To avoid a fall off in gas washing efficiency at lower flow rates, the scrubbers should not be oversized and two or more units in parallel are preferred to a single large unit.

Material of construction varies with the different installations. The hot gas piping is normally of stainless steel and the cool gas piping, after scrubbing, of mild steel or plastic. The Durban refinery has successfully used 3 mm thick mild steel piping for both the hot and cold gases with the hot pipe lagged to keep the temperature above the dew point. The scrubbers are usually of mild steel after bagasse burning boilers, although baffles and other wetted parts should preferably be of 430 stainless steel. In certain scrubber designs (Figure 1) the walls of the vessel below water level are lined with ceramic.

Chapman mentions that water containing silt or calcium carbonate can be used in the scrubber which then has to be of a suitable design to prevent blocking of nozzles etc. by solids. A local refinery is planning a modification to its flue gas scrubbing which now uses injection water to convert to neutralised final effluent. The volume of water required for

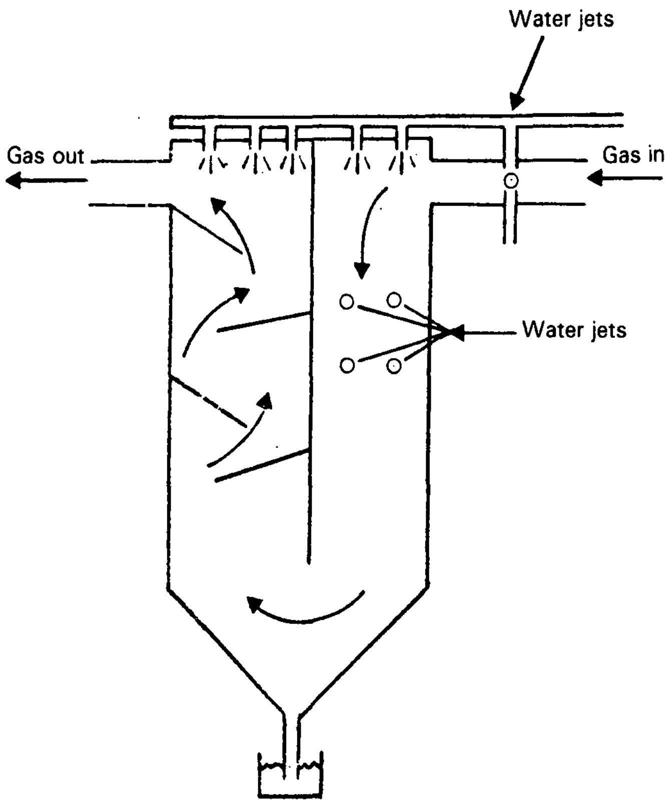

FIGURE 1 (a)

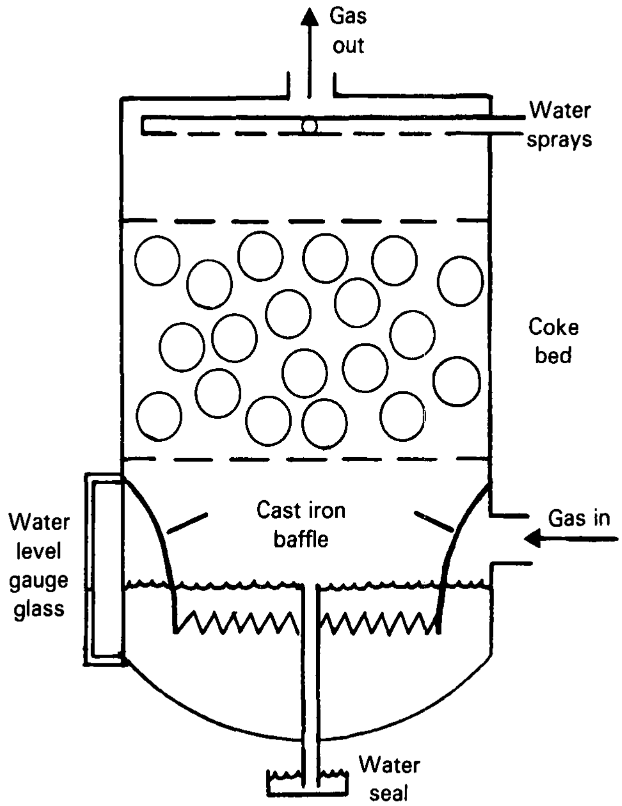

FIGURE 1 (b)

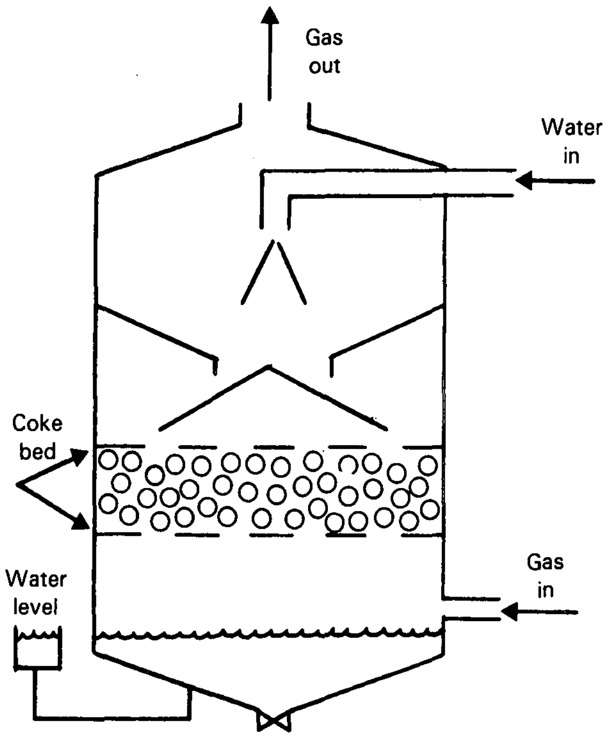

FIGURE 1(c)

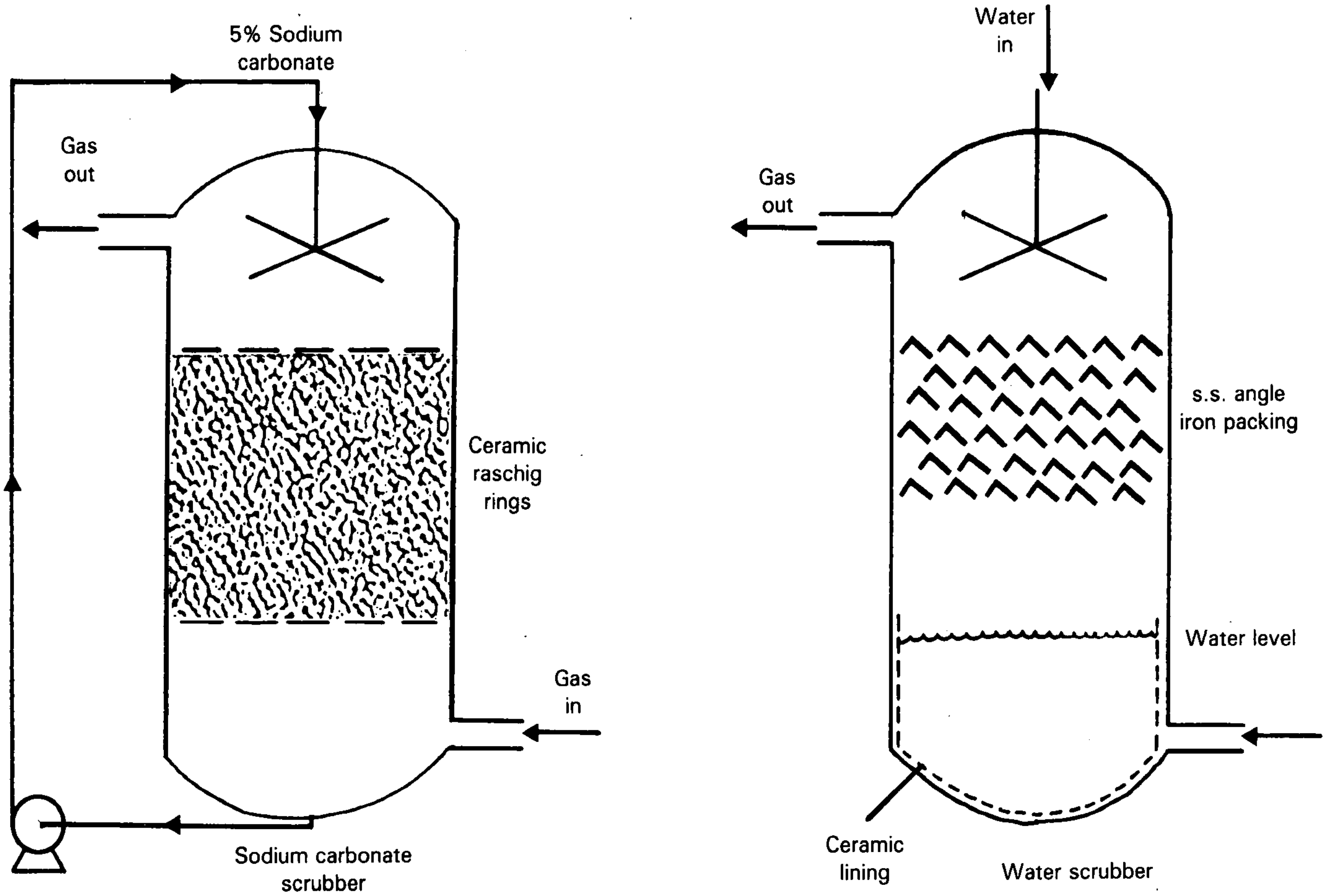

FIGURE 1 (d)

FIGURE 1 Sketches of various types of scrubbers found in refineries in southern Africa.

scrubbing is not quoted in any of the references which are available, but two local refineries use about 0,9 m³ per ton of sugar melted, equivalent to a gas to water ratio of about 100–150 to 1.

The function of the scrubbers is not only to clean the gas, but also to cool it and Alberino[1] suggests that the outlet gas temperature should be maintained at 50°C by adjusting the water flow rate. The South African refineries report a gas temperature of 50 to 60°C at the saturators. The lower the gas temperature, the higher the CO_2 supply at a given flow rate because of the effect of temperature on gas density, but the cooling effect of the gas in the saturators has to be compensated by a higher heat input through the saturator calandria.

A separator is required on the gas outlet from the scrubbers only if reciprocating compressors are used.

A sketch of the scrubbing plant at Dwangwa in Malawi is shown in Figure 2.

Compression

The compressors are installed between the scrubbers and the saturators. They keep the scrubbers under a slight vacuum, generally of the order of 25 to 50 mm of water. The delivery pressure depends on the friction loss in the piping and on the liquid head in the saturators. It is typically about 70 kPa at the saturators.

Various types of compressors are found in local refineries. For example, Gledhow uses reciprocating compressors (after a lime kiln), Malelane has Roots type blowers, while the other refineries use liquid ring compressors which are also recommended by Chapman and Hüse (in Ref. 1). These pumps are of all iron construction or with cast iron casing and stainless steel rotor and shaft. If the flue gas contains sulphur, it is recommended that the sealing water of liquid ring compressors be treated with sodium carbonate to maintain a pH of not less than 8. At the Durban refinery the carbonate solution from the scrubber is used as sealing liquid in the compressors.

The gas pressure and its carbon dioxide content should be constant at the saturators and since the carbon dioxide content of flue gas varies with the boiler loading, it is recommended that piping be provided to tap off flue gas from more than one boiler. The boiler with the most stable load should then be selected. The gas main from the compressors to the saturators should be provided with a pressure controller at the saturators, and with a by-pass opening into the gas pump suction to maintain a constant pressure. In the event of the pressure running too high, especially when the pH controller throttles gas to the saturator, the excess gas is recirculated. In some local refineries, the excess gas is bled to atmosphere by pressure release valves. Alberino[1] mentions that at Savannah refinery surplus gas is returned to the inlet of the scrubber.

The volume of gas required will depend on three main factors:

(a) The amount of lime added to the melt which in turn depends on the quality of the melt.

(b) The percentage of CO_2 in the flue gas after scrubbing.

(c) The efficiency of CO_2 use in the saturators.

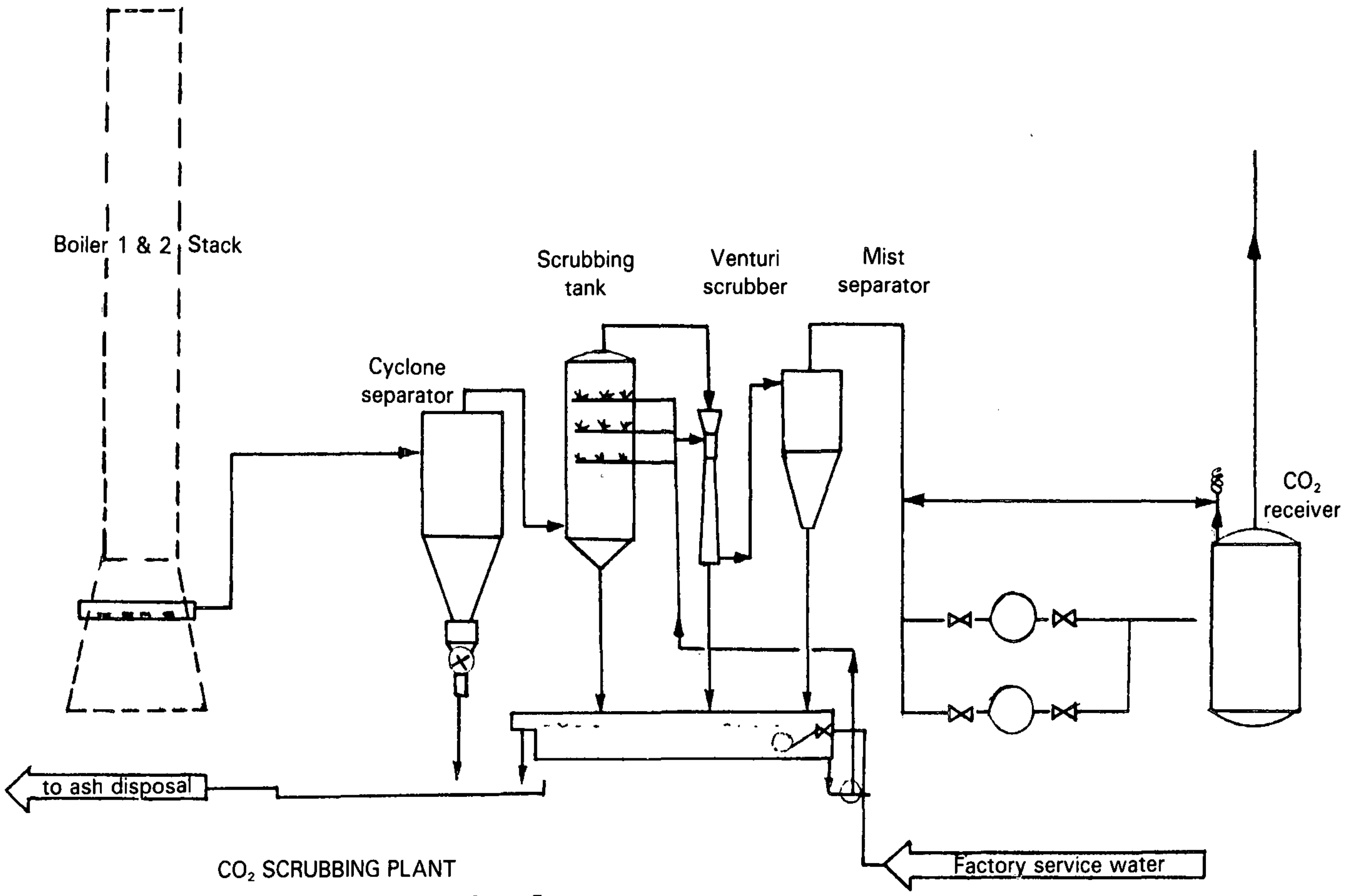

FIGURE 2 Flue gas scrubbing plant. Dwangwa Sugar Factory.

These factors are discussed below:

The stoichiometric requirement of CO_2 can be calculated from the formula:

$CaO + CO_2 = CaCO_3$

The amount of lime (CaO) required ranges from 0,4% to 1,2% on melt solids according to Chen.[3] Hulett Refinery reports values of 0,5 to 0,7 but, for design purposes, it may be safer to use a value of 1% especially if the refinery may have to process lower quality sugar than South African VHP.

The percentage of CO_2 by volume in flue gas is reported to average 12% at Malelane[5] with values as high as 16% before the boiler scrubber and 14% after the compressors. Occasional measurements at Ubombo and Hippo Valley indicate a CO_2 content of about 11 and 12% respectively, while the Tongaat-Hulett refinery (coal fired boilers) reports 10 to 11%. A value of 12% has been used in the gas volume calculation (Appendix 1).

The efficiency of CO_2 use is difficult to measure and although efficiencies of 100% have been claimed in line mixers,[3] both Huse and Chapman use values of 30% for conventional saturators. The efficiency will obviously be affected by the design of the saturators (number of units, gas distribution, liquid head) and by the brix and temperature of the melt.

The volume of carbon dioxide gas required for refining quoted by various authors is listed below:

Huse (in Ref. 2)	142 m^3 per ton of sugar in melt
Chapman (in Ref. 2)	162 m^3 per ton of sugar in melt
Alberino[1]	168 m^3 per ton of sugar in melt

Although the temperature and pressure of the gas are not specified, this volume can be assumed to be at approximately 50°C and atmospheric pressure. They should be compared to the 60 to 85 m^3 reported by the Durban refinery.

Flue gas requirements have been calculated in Appendix 1 for a refinery with a liming rate of 1% CaO on melt solids, a CO_2 concentration in gas of 12%, and an efficiency of CO_2 absorption of 30% in the saturators. The value obtained was 143 m^3 per ton of melt.

Summary and Recommendations

(a) Flue gas for scrubbing should be drawn from a boiler with a steady load to obtain an even concentration of CO_2 (about 12% by volume).

(b) With bagasse fired boilers a single water scrubber is sufficient. A gas to water ratio of 100 to 1 should be provided. Poor quality water can be used for scrubbing.

(c) A second scrubbing with 5% sodium carbonate solution is required for flue gas from sulphur containing fuels (coal or oil). The solution is recycled and the sodium carbonate requirements can range from 13 to 75 grams per ton of sugar melted, depending on the sulphur content of the fuel and the efficiency of the water scrubbing.

(d) The gas piping can be of mild steel, but the hot section must then be lagged to keep the temperature above dew point.

(e) Several designs of scrubbers are available. The scrubbers can also be of mild steel but wetted parts should preferably be of stainless steel.

(f) The gas after scrubbing should be at 50 to 60°C. With bagasse fired boilers a volume of 143 m^3 per ton of melt is adequate. Gas pressure at the saturators is about 70 kPa.

(g) Liquid ring compressors are recommended.

Acknowledgement

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APPENDIX 1

Calculation of CO_2 Requirements and Compressor Capacity

Assumptions:

(1) Maximum liming rate = 1% CaO on melt solids

(2) CO_2 concentration in gas after scrubber = 12%

(3) Water vapour concentration in gas by vol. = 8%

(4) Efficiency of CO_2 absorption in saturator = 30%

(5) Temp. gas after scrubber = 50°C

Basic formula $CaO + CO_2 = CaCO_3$

Molecular weights (40 + 16) + (12 + 32) = (40 + 12 + 48)

i.e. 56 + 44 = 100

Assume 100 tons of Brix in melt per hour

Wt. of CaO required = 0,01 × 100 = 1 ton h^{-1}

Stoichiometric wt. of CO_2 = $1 \times \frac{44}{56} \times 1000 = 786$ kg h^{-1}

Actual CO_2 required @ 30% efficiency

$$= \frac{786}{0{,}3} = 2620 \text{ kg h}^{-1}$$

$$= \frac{2620}{44} = 59{,}5 \text{ kg moles h}^{-1}$$

@ 22,4 m^3/mole gas volume = 59,5 × 22,4 = 1333 m^3 h^{-1} at STP

Flue gas requirement after correction for temperature, CO_2 and water vapour content

$$= \frac{1333}{0{,}12} \times \frac{1}{0{,}92} \times \frac{(273 + 50)}{(273)}$$

= 14285 m^3 h^{-1}

or 143 m^3/ton brix in melt