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ABATEMENT OF HYDROGEN CHLORIDE IN STRUCTURED PACKINGS

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ABSTRACT

The abatement of Hydrogen chloride is one of the most important problem in geothermal fields. If hydrogen chloride concentration exceeds 15-20 ppm, steam washing is necessary to prevent corrosion. The abatement mechanism in conventional washing systems is not completely understood. This paper analyses the use of high efficiency structured packings. For this type of packings there is little open literature so a pilot plant has been designed and built. New correlations to compute mass transfer coefficient and pressure drop have been proposed.

INTRODUCTION

In high enthalpy geothermal fields, superheated steam is transported from well-head to the utilizing plant by insulated pipelines.
Where the insulation is incomplete or inadequate, and generally everywhere steam temperature drops, condensation occurs. The presence of HCl in geothermal steam, which has been deeply investigated[1], enhances corrosion because it acidifies the condensate. For this reason steam washing in geothermal plants is a common practice, whenever the HCl concentration exceeds 15-20 ppm.
Conventional techniques of steam washing consists of an injection of caustic soda solution in the pipeline followed by a cyclone separator, which removes droplets of solution and condensate from steam.
In the Geysers area, corrosion mitigation system is done by injection of caustic soda near the cyclone separators for superheated steam, or directly at the well-head, if steam is close to saturation conditions[2].
Other authors[3/4] describe the results obtained from a two stage injection system, in which injection and mixing spools were designed to obtain high mass transfer from steam to liquid phase.
Macker and Hizlip[5] used multiple injection nozzles, their water injection volume was set at a specific flow of 1% by weight, and soda amount for maintaining pH values around 8-8.5.
A system using a static mixer after the caustic soda solution injection and cyclone separator is used by ENEL in Larderello [6].
Absorption of hydrogen chloride depends on several factors: interfacial steam-liquid areas, driving force and mass transfer coefficient.
Conventional washing systems seem to provide low mass transfer coefficients because of the low slip velocity between steam and liquid. Moreover, in those systems, interfacial areas do not appear high and the residence times short.
For these reasons use of structured packings seems to be an attractive alternative to the conventional washing system. In fact these types of packings are characterised by low liquid loads, high efficiency and extremely low pressure drops.
In the range of concentrations of our interest, the solubility of HCl in water is extremely high and mass transfer resistance in the liquid phase is negligible. For this reason the overall mass transfer coefficients for countercurrent and for cocurrent arrangements are not very different.
In this work a cocurrent flow has been used because of it can operate with high gas velocity without any problem of flooding. Operating with high gas velocity allows use of a small diameter column and high mass transfer coefficient.
The goal of this work is evaluation of mass transfer coefficient, overall efficiency and pressure drop for a structured packing column. For this reason a pilot plant has been designed and built.

DESCRIPTION OF THE EXPERIMENTAL LOOP AND TEST EXECUTION

A schematic diagram of the loop is reported in Fig 1. As can be seen, the pilot plant consists of various pieces of equipment which are used for the three possible configurations of the plant. It is possible to operate with two main contacting devices, an absorption column, which can work cocurrently or countercurrently, and a static mixer.
In this work the results obtained with the column working cocurrently are presented. In Fig. 2 the configuration used has been shown.

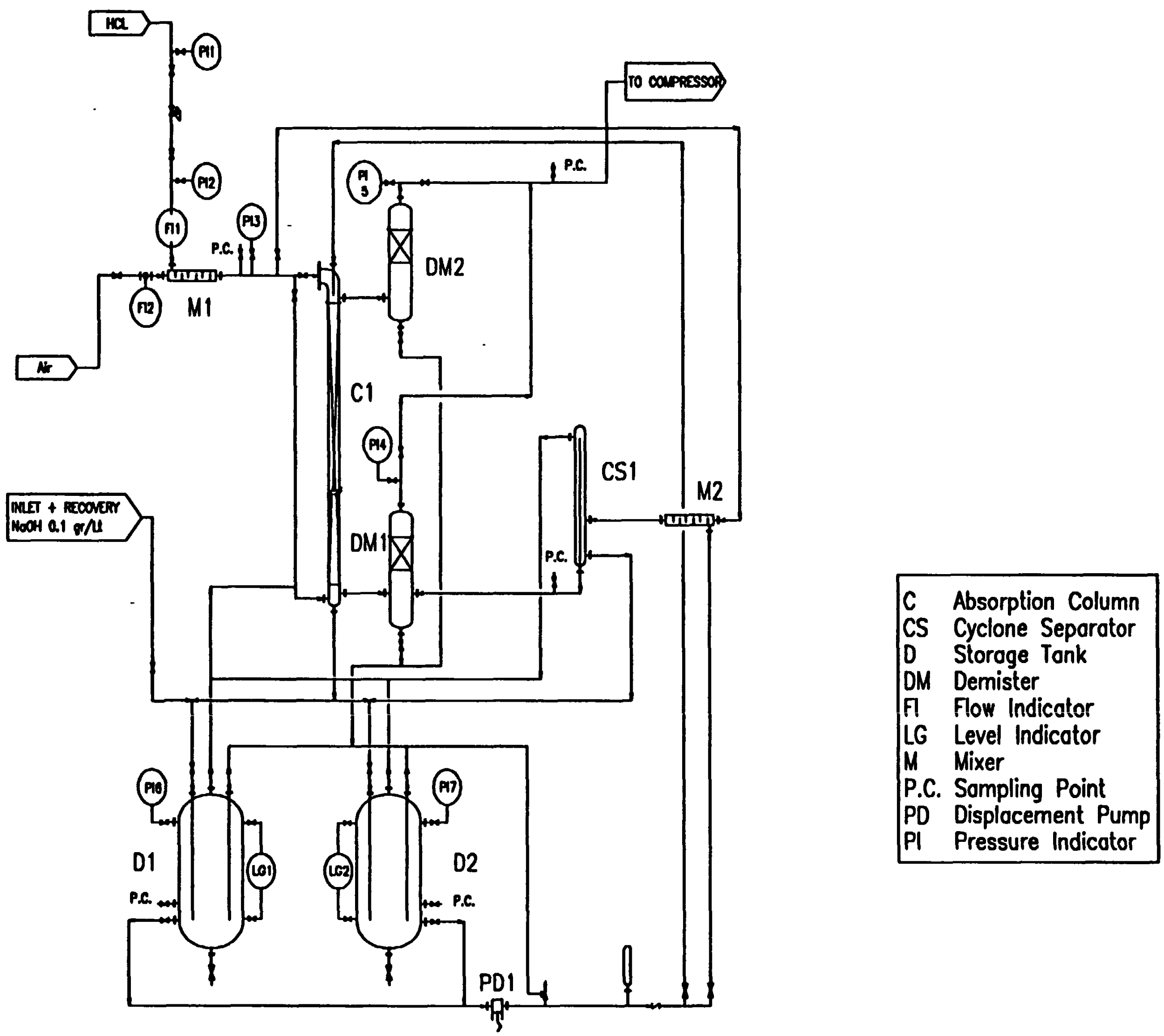

Fig. 1 Schematic diagram of the loop

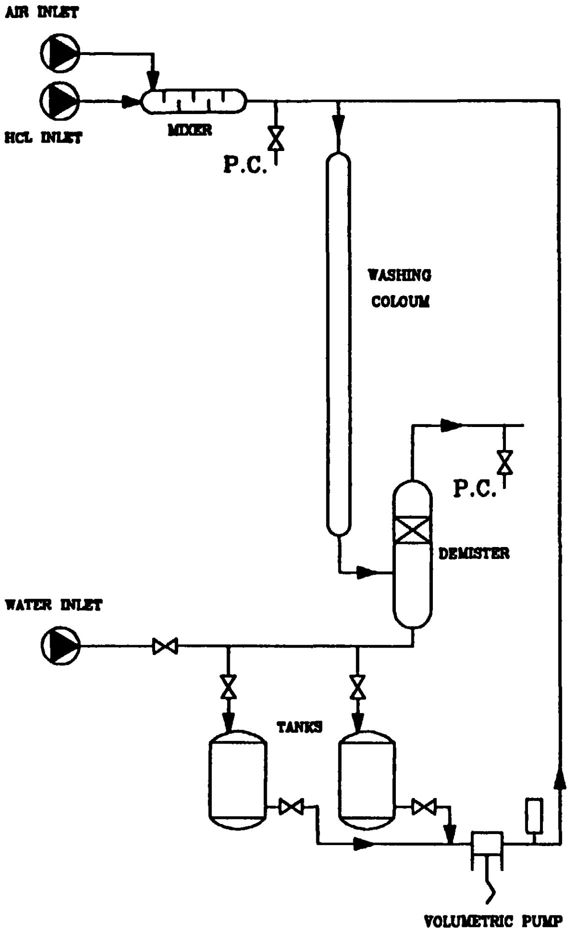

Fig. 2 Schematic diagram of the cocurrent arrangement

Compressed air flow rate is measured by a vortex and controlled by a pneumatic valve. Hydrochloric acid, 99% purified, is supplied by a gas cylinder. Both the pressure reducing valve on the cylinder and the flow meters are designed withstand in the corrosive action of HCl. The HCl flow meter, made by HI-TECH, is based on the principle of heat transfer along a heated section of a capillary pipe. The instrument is particularly flexible, as it can work within wide ranges of both pressure and temperature without any appreciable influence on the accuracy of the mass flowrate.
Compressed air containing a selected amount of HCl is fed to abatement equipment (C1). The column, 5 centimeters internal diameter and 4 meters long, is filled with a structured packing by Sulzer, type BX, that allows it to operate with very low liquid loads.
The basic solution (with soda concentration of 4 g/l), pumped from feed tank D1, is sent to the top of the column where the washing operation occurs, after the HCl absorption, this solution is discharged in tank D2.
Cleaned gas flows through a wire mesh demister (DM1) for abatement of entrained drops and then is discharged to the atmosphere.
Just before the column inlet a gas stream of 60 l/h is sampled and is sent to three bubbling traps in series; each of those contains 100 ml of NaOH 0.1 N. Another sampling section is also located on the demister gas outlet.
Analysis of traps solution are performed by a mass spectrometer, according to conventional Cl^- industrial water analysis. The collected samples, prepared with the appropriate agents (solutions of $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$, Hg(SCN) and NAOH 0.1 N) are compared with the blank sample (NaOH 0.1 N) in order to read the absorbance value.
Sensitivity of the trace level chloride analysis (2 µg of HCl for 1 ml of solution) imposes the working time necessary to each experiment. The data of this work have been obtained with experiments 1-4 hours long, depending on HCl concentration.

EXPERIMENTAL RESULTS

The efficiency of the column has been defined as

$$\eta = \frac{(C_{in} - C_{out})}{C_{in}} \qquad 1)$$

where C_{in} and C_{out} are the concentration of HCl in the inlet and in the outlet stream.
In Fig. 3 is shown the efficiency of the column as a function of the gas flowrate. The efficiency increases with high liquid load and decreases with high gas flowrate. The reason being that with high liquid load, the interfacial areas increases, while with high gas flowrate the residence time decrease.
Fig. 3 shows the existence of a limit value of the superficial liquid velocity below which the efficiency decreases abruptly.
In Fig. 4 the dependence of the efficiency from the liquid velocity is shown. For the packing used in this work, with 4 m/s superficial gas velocity, the limit below which the efficiency decreases abruptly appears to be about 1.5 $m^3/m^2/hr$.

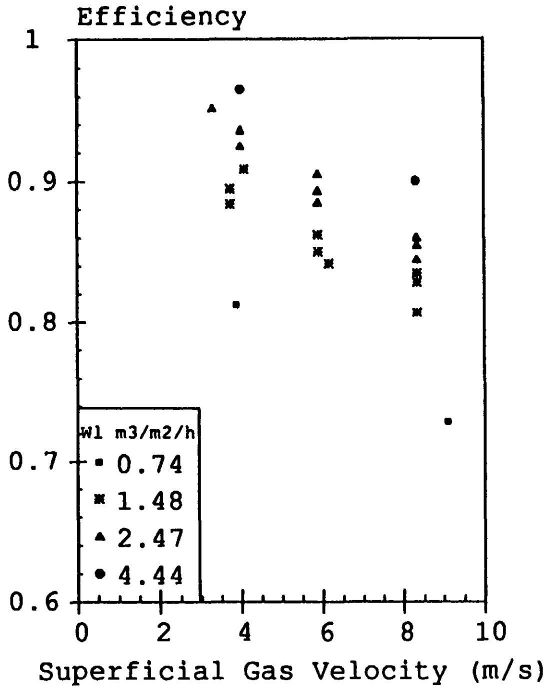

Fig. 3 Effect of the superficial liquid and gas velocity on the experimental value of the efficiency

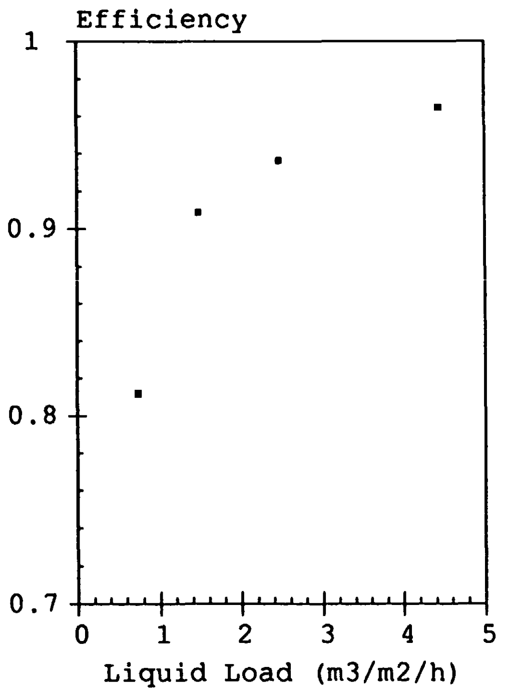

Fig. 4 Effect of the superficial liquid velocity on the experimental value of the efficiency. Superficial gas velocity 4 m/s

Efficiency

The mass balance can be written in the form

$$G \cdot dy = k_g \cdot A \cdot S \cdot (y - y') \cdot dz \quad (2)$$

where G is the molar flowrate of the washed gas, y is the molar fraction of HCl in the gas, y' is the molar fraction of HCl at the interface surface, k_g is the gas film transfer coefficient, A is the surface of interface per unit volume of column and S is the column section.
As resistance to the mass transfer coefficient in the liquid phase is negligible/7/ it is possible to rewrite Eq. 2 to calculate the experimental value of the product K_g A.

$$K_g \cdot A = \frac{G \cdot \ln\left(\frac{C_{in}}{C_{out}}\right)}{S \cdot H} \quad (3)$$

Where H is the column height.
From the analysis of the data it is possible to compute the experimental value of the product K_gA.

A number of different correlations to calculate the value of gas film transfer coefficient are available in literature. Sherwood et al./8/, for the wetted-wall columns, and Bravo et al./9/, for the structured packings, assumed that

$$K_g \propto \left(\rho_g \cdot W_g\right)^n \quad (4)$$

where n is equal to 0.77 in the first case and 0.8 in the second case. For the packed towers other authors used correlations like Eq. 4 with a different value of the coefficient n. Semmelbauer/10/ proposed n=0.59 while Morris & Jackson/11/ assumed n=0.75.
The influence of the liquid flowrate on the surface of interface per unit volume is more complex. Some authors, like Norman/12/, using grid-packed towers, showed the independence of A from liquid rate. Other authors like, Borden and Squires/13/, using ring packed towers, proposed

$$A \propto W_l^{0.4} \quad (5)$$

This analysis shows that the dependence of A by the liquid flowrate is a strong function of the type of packing used. For metal structured packings Spiegel et al./14/ suggests

$$A \propto W_l^{0.2} \quad (6)$$

Using literature analysis results for metal structured packings, it is possible to calculate the product K_gA as

$$K_g \cdot A = C \cdot \left(\rho_g \cdot W_g\right)^{0.75} \cdot W_l^{0.2} \qquad (7)$$

The value of the constant C must be evaluated from experimental data. In this case, using minimum square roots method, results C=0.159.
In Fig. 5 a comparison between calculated and experimental value of K_g A is showed.

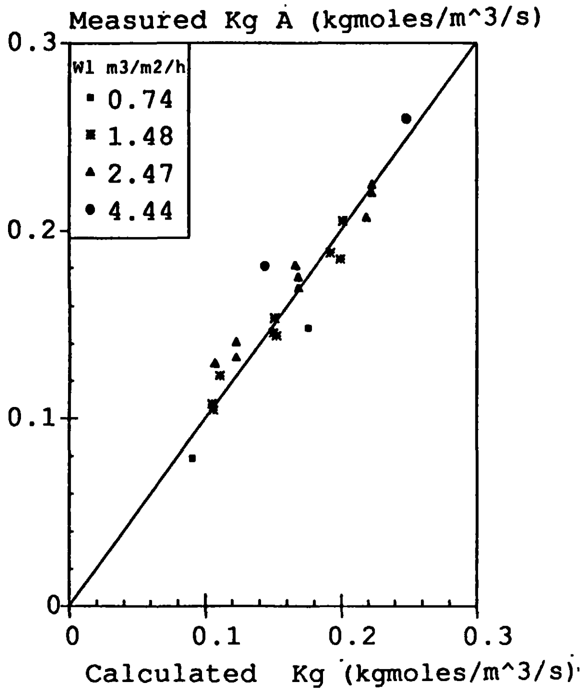

Fig. 5 Comparison between calculated (Eq. 7) and measured K_gA.

There is good agreement between the calculated and the measured value of the product K_g A , but a close examination of the figure shows that the dependence from the liquid load is a little bit greater than that proposed by Spiegel.

Pressure Drop

A number of empirical correlations or theoretical models are available in the literature. In a recent work Bravo et al.[15] proposed to calculate pressure drop in structured packing as the gas phase flows in a pipe. According to these authors the effect of the liquid phase is accounted only for the reduction of the space available for the gas phase.
In Fig. 6 our experimental value of the liquid hold-up, as a function of the superficial gas velocity, are shown. It is noticable that, in all the experiments, this parameter remains below the value of 1 %. so that the reduction of the section available for the gas phase is negligible. For this reason, in this work, the influence of the liquid rate on the pressure drop has been neglected.

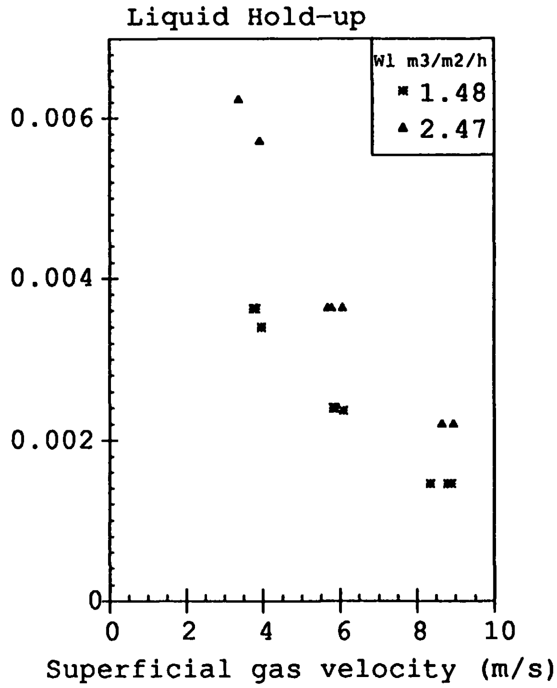

Fig. 6 Effect of the superficial liquid and gas velocities on the experimental value of the liquid hold-up. Gauze Packings

The pressure drop has been computed with no liquid present as proposed by Bravo et al.

$$\Delta P = f \cdot \frac{\rho_g}{d_e} \cdot W_{ge}^2 \qquad (8)$$

where f is the friction factor, ρ_g is the gas density, W_{ge} is the effective gas velocity inside the flow channel, and d_e is the equivalent diameter.
The effective gas velocity can be computed as

$$W_{ge} = \frac{W_{gs}}{\left(\varepsilon \cdot \sin(\theta)\right)} \qquad (9)$$

where W_{gs} is the superficial gas velocity, ε is the packing void fraction and θ is the angle of inclination of flow channel from the horizontal.

The equivalent diameter of the channel can be assumed equal to the side of corrugation or crimp of the packing./15/ Bravo et al. introduced the Eq. (10) to compute the friction factor in the channel.

$$f = C_1 + \frac{C_2}{Re_g} \quad (10)$$

where the Reynolds number is defined as

$$Re_g = \frac{d_e \cdot W_{ge} \cdot \rho_g}{\mu_g} \quad (11)$$

and the constants C_1 and C_2 are particular for each type of packing used. These authors assumed C_1=0.171 and C_2=92.7; our experimental data show different values for these constants. Probably this difference can be attributed to the different material of the packings, in fact most of the data of Bravo are obtained with gauze packing while our data are obtained with metal packings.

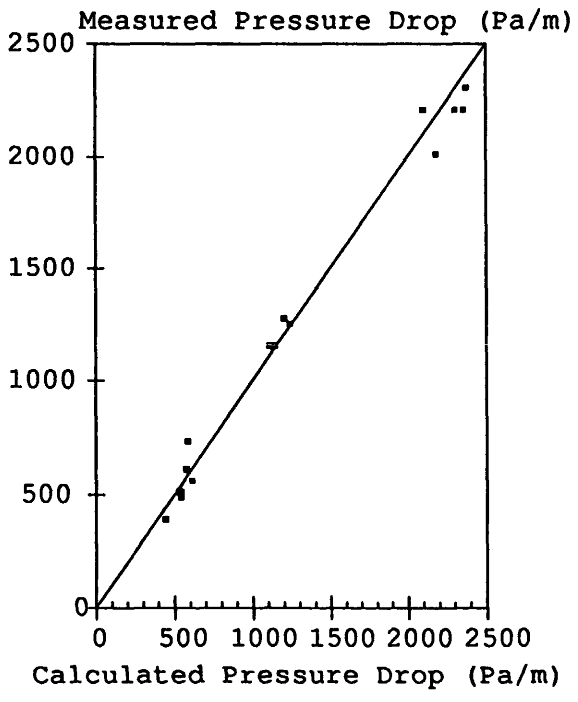

Fig. 7 Comparison between calculated (Eq. 8) and measured pressure drop.

Fig. 7 shows the comparison between the experimental data and the computed data obtained assuming C_1=0.085 and C_2=181.3. There is good agreement between calculated and measured value of the pressure drop if the constants C_1 and C_2 suggested in this paper are used. If instead the values proposed by Bravo et al., are used in all the range of gas flowrate, the measured pressure drop are over predicted.

CONCLUSIONS

A structured packing column, working in cocurrent flow, has been tested to determine its efficiency for HCl abatement

- Efficiency seems to be high for low liquid flowrate (1.5-2.5 $m^3/m^2/hr$)
- Pressure drops are very low for gas velocity in the range of 4 and 10 m/s

The experimental data indicates this type of arrangement allows operation with high gas velocity and high abatement efficiency too. This result is particularly important because it shows that it is possible to operate with very small internal diameter columns.

- Some experimental data have been obtained using a lack of Soda in comparison with the stoichiometric value necessary to neutralize the HCl absorbed.

In these cases the efficiency also remains high. This can be explained by the shape of the equilibrium curve of the HCl-H_2O system in the range of low HCl concentration. For this reason the presence of Soda in liquid phase is very important, not for chemical equilibrium, but only to mitigate corrosion phenomena

ACKNOWLEDGEMENTS

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NOMENCLATURE

A	surface of interface per unit volume
C	Constant Eq.7
C	HCl concentration
de	equivalent diameter of a channel
f	friction factor
G	molar flowrate of washed gas
H	column height
k_g	gas phase mass transfer coefficient
K_g	overall mass transfer coefficient
Re_g	gas Reynolds number
S	column section

W_g superficial gas velocity
W_{ge} effective gas velocity
W_l superficial liquid velocity
y molar fraction of HCl
ΔP Pressure drop for unit height of packing
ε packing void fraction
η efficiency
θ angle of flow channel based on horizontal
μ gas viscosity
ρ_g gas density

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