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Pilot Testing of a Dry HCl Abatement Process for Geothermal Steam

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In many geothermal areas, an abatement of hydrochloric acid present in the steam is essential in order to produce energy before turbine expansion. In fact, concentrations of acid higher than 5 ppm risk seriously corroding the turbine, significantly increasing the costs of this energy source. In 2018, Enel Green Power decided to support a research project, called Georockwash, and aimed at identifying a new process for the abatement of HCl in geothermal steam with the collaboration of Magona Technological Pole, as a centre specialized in the experimentation of industrial processes on a pilot scale.
The project has developed a new abatement process based on the use of dry $CaCO_3$, as agent for the neutralization of acid. The process has been tested initially on a laboratory scale and then on a pilot scale with the construction of a 500 kg/h steam plant, skid mounted and transportable.
The experimentation campaign on the pilot plant was conducted first at the facilities of the Magona Pole and then at an Enel Green Power geothermal power plant. In the experimentation the effects of the main operating parameters on the abatement efficiency were evaluated and correlated with a semi-empirical equation.
Finally, the experimentation showed abatement efficiencies often higher than 95%, confirming the suitability of the new process for geothermal use with low investment and operating costs.

1. Introduction

In Italy, the energy exploitation of geothermal steam takes place mainly through thermodynamic cycles with direct turbine. The steam collected from the wells goes direct to the turbine. Geothermal steam contains significant quantities of CO_2 and traces of SO_2, Hg, H_3BO_3, HCl, Silica.
Generally, the steam goes, as it is, from the well to the turbine, postponing the removal of pollutants to treatments after the expansion in turbine. An exception to this practice is when the HCl concentration exceeds 5 ppm, generating a risk of corrosion for the turbine itself. In such situations, washing with basic solutions with high removal efficiency is used, but with the disadvantage of eliminating the superheating present in the steam. The loss of superheating results in a reduction in thermodynamic efficiency in the turbine of 3 to 5% (Culivicchi,2005). Hence the keen interest in identifying new dry HCl removal processes to maintain the degree of superheating.
In 1992, Hinzt et al. found that solid alkaline compounds, such as sodium carbonate and sodium borate, could absorb up to 90% of the HCl present in superheated geothermal vapours. This phenomenon had been observed in some disused geothermal wells, where solid residues from previous alkaline washing had remained. Gallup (1998) investigated the removal of HCl in steam by boiling HCl solutions and then passing the steam through columns containing various types of solids. Gallup obtained significant HCl removals with both strongly basic solids and calcium carbonate.
In 2009, the US Department of Energy funded Calpine Corp. to experiment calcite beds about 1 m high in geothermal wells in California. The trial showed that regardless of the initial HCl concentration, the concentration at the outlet was always less than 2 ppm (+/- 1 ppm).

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Since 2018, CPTM laboratories experimented various dry treatment processes using lime, sodium bicarbonate and sodium carbonate. Among these processes, sodium carbonate is the most economical reagent, maintaining good hydrochloric acid abatement efficiencies. During use, the carbonate tends to deactivate before its complete reaction. Tests have shown that it is possible to reactivate the carbonate by water washing.

Enel Green Power (EGP) shown interest in the carbonate process and decided to carry out a pilot plant trial. EGP choose to realize the pilot plant in partnership with CPTM. The pilot plant has been designed to treat 500 kg/h of steam at 8 bar and with an input concentration of 100 ppm HCl. The plant consists of two columns, which work in an alternative way: one column in operation and the other in stand-by mode. When the column in operation loses its effectiveness, the plant exchanges the two columns, maintaining continuity of operation. The column in stand-by can perform a regeneration cycle, which prepares it for its next use. The entire system is mounted on a transportable skid, which has enabled it to be set up first at the CPTM research centre and then put into operation at the EGP plant in Monteverdi, in the province of Pisa. Figure 1 shows the pilot plant during construction. The plant is equipped with a flow and pressure control system, which allows exploring various operating regimes.

Figure 1: Pilot plant during construction operations

2. Pilot plant description and operation

The system is composed of two columns inside which there is the bed of reagent that is crossed by the steam. The working principle foresees that the reagent bed constituted by the mineral $CaCO_3$ reacts with HCl contained in the steam in gaseous state generating the reaction product $CaCl_2$ in solid state. As the reaction progresses, the ore must be washed with a stream of water to remove the reaction product. To have continuous operation, while one column is running, the other column undergoes bed regeneration (see Figure 2).

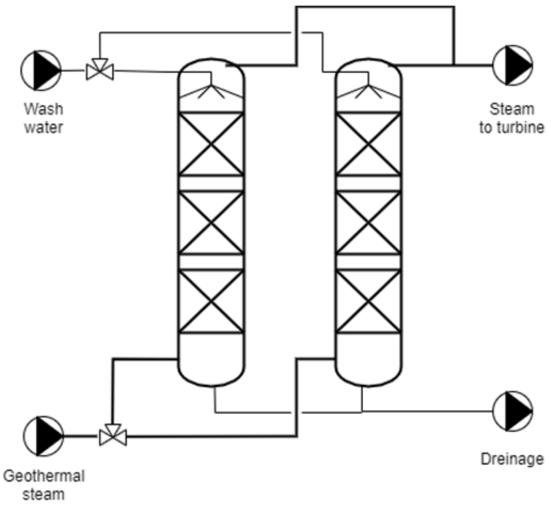

Figure 2: Conceptual diagram of the pilot plant

The system also provides for the possibility of sending to the column in regeneration a current of cold air before washing, to cool the bed, and a current of hot air after washing to dry the bed and heat it in order to avoid condensation at the return of steam.
The pilot plant is built on a skid and is transportable in situ to treat a steam stream from the steamer. The connection to the plant is by flanged connection.
The columns can hold 550 - 600 kg of limestone with a grain size of 30-60 mm.

2.1 Plant start-up and shutdown

To reduce steam condensation, the system is designed to send hot air during start-up to the column and cold air during steam shutdown, before flushing.
Atmospheric air is sucked in by a fan and heated by finned electric coil up to 200°C. At the inlet and outlet of the exchanger there are two temperature gauges. The power of the exchanger is regulated by the outlet temperature. The column air inlet and outlet are regulated by automatic valves.

2.2 Normal operation

The plant has been designed to treat a steam stream from 250 to 500 kg/h.
The flow rate is controlled by an automatic valve connected to a volumetric flow meter, located on the steam inlet pipe to the columns. Upstream of the flow meter are a pressure gauge and some temperature gauges.
Subsequently, on the inlet pipe, a sample inlet is provided to carry out the HCl concentration measurement at the plant inlet, before branching to the twin columns C1 and C2.
Along the column there are ten temperature gauges and sample inlets for steam analysis.
The column has also an electric heaters controlled by the external wall temperature.
The outlet piping from the columns, before coming together in a single pipe, includes a pressure gauge and relief valve set at 12 bar.
The plant pressure is regulated by an automatic valve, which is connected to a pressure gauge.

2.3 Bed regeneration

The fixed bed can be washed with water to achieve regeneration. The water is taken from a tank outside the skid. The water is fed to the column in regeneration with a pump. The flow rate is measured with an in-line rotameter. Two sample inlets are provided at the outlet of the columns for wash water analysis.

3. Experimental results

The experimentation involved the continuous operation of the pilot plant. Two continuous experimental campaigns were carried out, the first was carried out in the period 11/12/2019 - 20/12/2019, while the second was carried out in the period 04/02/2020 - 03/03/2020.
The first campaign of tests, in addition to providing the first experimental results, was useful to identify operational criticalities of the test procedure and sampling method. Therefore, the second campaign was conducted to validate the first, repeating the most significant operating conditions and refining the operational methodology. The tests were aimed at finding out the effect of operating parameters on abatement efficiency. In particular, the effect of bed grain size and steam pressure was investigated at various flow rate, according to the values shown in Table 1.

Table 1: Parameters investigated

Parameter	Range	Units
Size	34 - 50	mm
Pressure	4 - 8	bar
Flow rate	300 - 700	kg/h

It should also be noted that the inlet HCl concentration was highly variable in the different tests, to the point that in some samplings the inlet concentration varied by more than 50% within an hour. The measured values were in the range of 90 to 130 mg/L. The mean value was 117 mg/L. Values less than 90 mg/L and greater than 170 mg/L were not considered when calculating abatement efficiency.

3.1 Size effects

The two columns were filled with two different grain sizes of $CaCO_3$. One column with finer grain size with average value 34 mm and the other with larger grain size with average value 50 mm. The tests were then repeated at various flow rates. Even though the geothermal well has a steam with a constant temperature, the thermal dispersion of the plant implies a temperature variation also in the bed. Higher steam flow rates are associated with a higher average bed temperature. Thus, we went from an average temperature in the bed of 180°C for a flow rate of 300 kg/h to 200°C for a flow rate of 500°C.
Figure 3 shows the trend in abatement efficiency for the two different particle sizes as the flow rate varies. It can be seen that a lower particle size of the bed corresponds to a higher abatement efficiency at the same flow rate. This observation is congruent with the greater surface area per unit volume possessed by the bed with a smaller grain size.

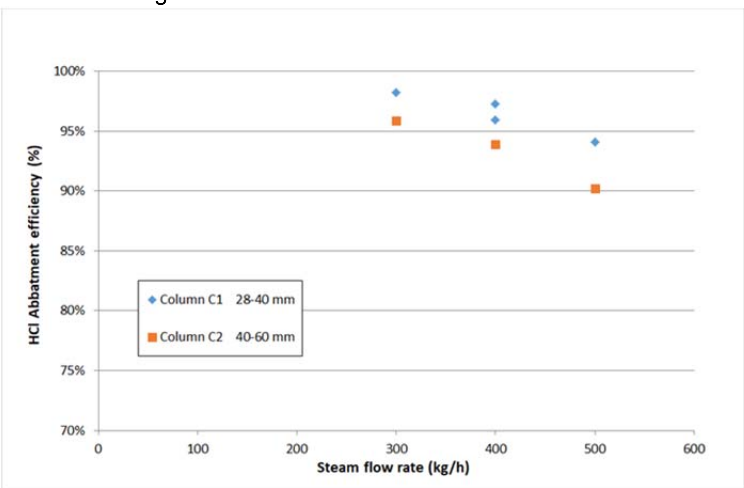

Figure 3: Abatement efficiency for different grain size for various flow rate at constant pressure.

3.2 Pressure effects

The effect of pressure on abatement is significant. Figure 4 shows the effect of pressure on abatement at the same flow rate (500 kg/h) for the two different bed grain sizes. We can notice that as the pressure increases, the abatement efficiency also increases. These data indicate that steam pressure is one of the driving forces behind the abatement process.

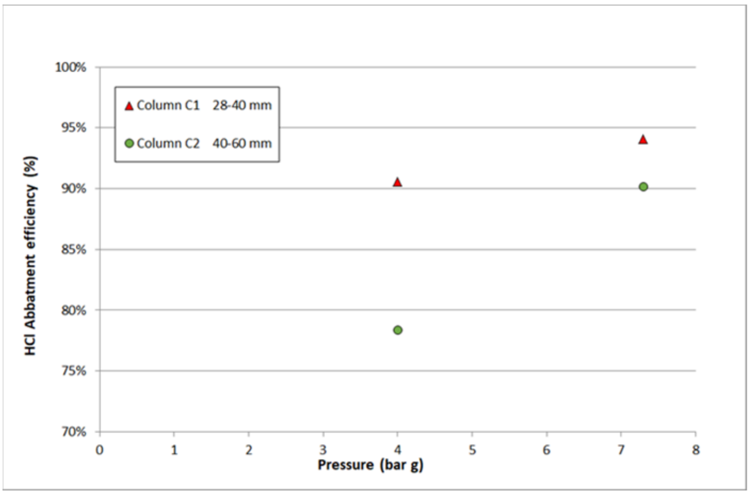

Figure 4: Abatement efficiency for different pressures for various flow rate.

4. Mathematical modelling

Referring to the experimental measurements, a mathematical model has been created to correlate the HCl concentration profile in the column with the variation of operating conditions: pressure, temperature, flow rate, type of filling. The model chosen is a semi-empirical model, in which the reaction rate of HCl is assumed directly proportional to the surface area of the bed and exponentially related to its concentration. As shown in equation (1), where there are the reaction rate, v, defined as the mass of HCl reacted in the unit in the reference volume, k proportionality constant, A_{sup} surface area of the bed, C volumetric concentration of HCl and n exponential coefficient of concentration. Thus, the model has only two parameters, the coefficient k and the exponent n, to be fitted with experimental measurements.

$$v = k\,A\,C^n \qquad (1)$$

$$u\,A\,C(z) = u\,A\,C(z+dz) + k\,C^n\,a\,A\,dz \qquad (2)$$

$$\frac{dC}{dz} = -k\,\frac{a}{u}\,C^n \qquad (3)$$

$$\frac{dR}{d\zeta} = -k\,\frac{a}{u}\,C_0^{n-1}\,R^n \qquad (4)$$

Where: $\zeta = \frac{z}{H}$, $R = \frac{C}{C_0}$, $C_0 = C(z=0)$ $=>$ $R(\zeta = 0) = 1$

Employing Equation 1 on an infinitesimal section of the column, it can perform the mass balance and derive the differential equation corresponding to a stationary condition.

Equation 4 is the dimensionless ordinary differential equation at a known initial condition derivable from the mass balance expressed in Equation 2. In Equation 4, H is the bed height, C_0 the initial pollutant concentration, and a the specific area of the fill ($A_{sup}/V_{reactor}$). Equation 4 can be solved numerically by fixing the values of the two parameters k and n, while H , C0 and a are terms of the various experimental conditions actually tested.

The choice of the optimal values for parameters k and n was made by minimizing the error between the values of R predicted by the model and those measured in the experimental campaign. The metric chosen of which to minimize the error is the mean gamma deviance.

The minimum deviance value obtained is 0.37, with k = 6.1-103 (using SI units and C0 in g/m3) and n = 2.0.

Figure 5 shows the values of R = C/C_0 predicted by the model in relation to those measured in the experiment. The points above the central line represent an estimated value that is higher than the measured value and thus a higher concentration value than is present in the column. The two dashed lines delineate the calculated values that are between half and twice the measured values.

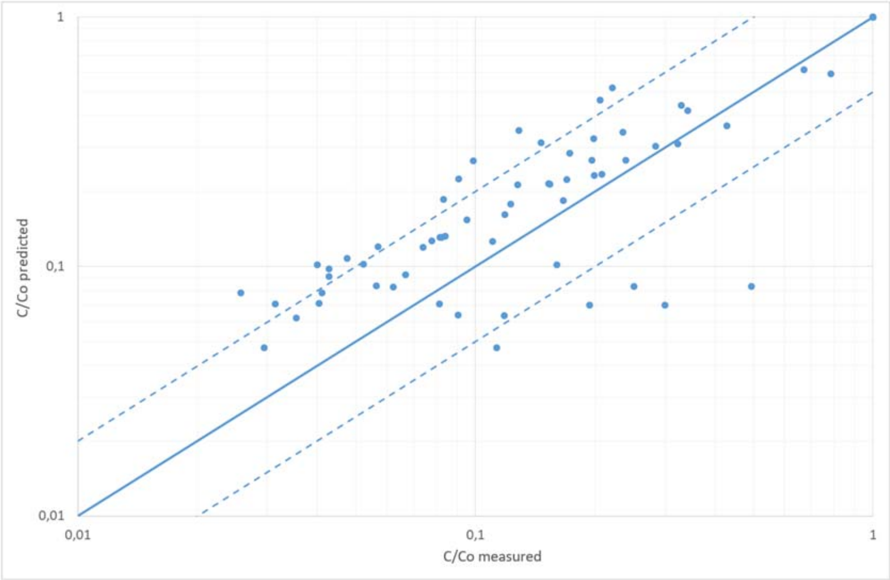

Figure 5: Model-predicted values versus measured values.

5. Conclusions

The experimentation has shown that the new process can guarantee high abatement efficiencies of the HCl contained in the geothermal steam, using a reagent much cheaper than the caustic soda normally used.
Optimizing the process parameters, it is possible to obtain abatement efficiencies higher than 95%. In particular, the high pressures typical of geothermal steam favour abatement, as does the use of fillings with a smaller grain size.
This first industrial experimentation is the basis for further full-scale experimentation of the new process in the geothermal field and in other areas with similar problems of corrosion by hydrochloric acid.

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