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Characteristics and Performances of Chlorine Scrubbing Systems in the Larderello Area

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ABSTRACT

The geothermal fluid originated from the deep wells in the Italian geothermal fields can be rich in chlorine compounds, and its preliminary abatement, both with in well treatment and with surface equipment, plays a significant role in prolonging the industrial life of gathering systems and turbines.

pH control in the discharge of chlorine abatement plants is a key task in the control of plant efficiency and chemical consumption optimization. The high salinity, the presence of hydrogen sulfide and the high temperatures of residual waters prevent adoption of conventional instrumentation. For this reason Enel has built a special assembly capable to adapt high performance pH-meters to chlorine abatement plants. In this paper we report the achievements reached and data of the equipments currently working in more 5 plants.

1. INTRODUCTION

Corrosion in geothermal pipelines and turbines is mainly originated by chloride compounds, present in the steam as hydrogen chloride (HCl) and ammonium chloride (NH4Cl) (Bracaloni[i] et al. 1995).

The chloride ion, when carried by the above-mentioned species, is formed in the presence of small amounts of condensed steam at dew point and can induce massive corrosion phenomena at high thermal dispersion points and at the turbine dew point. Chloride corrosion can generate severe damages by pitting and stress-corrosion mechanisms. The condensed phase can reach very high chloride concentrations and pH values of 2 – 4, depending on the chloride content in the vapor phase. The pH in the fully condensed phase, although different owing to variations in ionic species concentration, is mainly affected by the chloride content.

Although other chemical components of geothermal fluids and their thermodynamic features can synergistically affect corrosion, chloride concentration in the steam is the driving force for most corrosion phenomena currently observed in geothermal plants. This has been experimentally demonstrated by direct corrosion rates on geothermal steam. In these studies a linear correlation between Chloride concentration and dew point corrosion rates has been verified[ii]

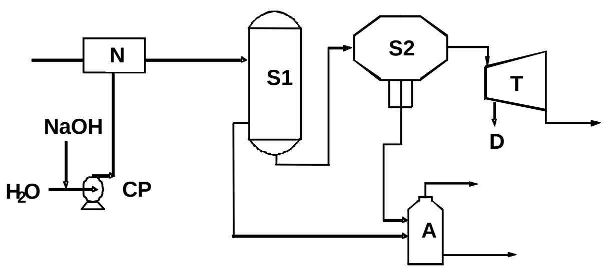
Corrosion mitigation in the Enel power plants is performed by steam scrubbing systems. The chloride abatement is achieved by cooling steam to saturation and keeping steam quality between 95-98%. The chloride is transferred to water due to the high affinity of Hydrogen Chloride and ammonium chloride for this phase. Presence of Sodium Hydroxide in scrubbing water solution prevents formation low pH water recovery. The water used for abatement is usually from geothermal plants; the Redox Potential and oxygen absence prevent further parallel corrosion reactions. The resulting hot waters from abatement plants contain the chlorine species neutralized as Sodium Chloride and other soluble species such as boric salts. One of the most significant tasks in the abatement plant performance control is the measurement of the discharge water pH. An accurate and reliable control of the pH is necessary in order to prevent sub-stoichiometric NaOH dosing and formation of acidic discharges and also an excess dosage. In the latter case boric acid buffering effects can induce large consumption of NaOH without appreciable pH variations. To solve these problems Enel has performed studies in order to set-up a reliable system for pH discharge control which is described in the following paragraphs.

2. GENERAL STRUCTURE OF CHLORIDE ABATEMENT PLANTS

The general structure of steam scrubbing chloride abatement plants is described in Fig.1 and 2 is composed of four modules:

1. A Spraying nozzle for scrubbing solution injection
2. A mixer line and pipeline
3. A cyclone separator
4. A vane type demister

The equipment varies greatly from one geothermal plant to the other for section 1 and 2 structure while separator section is quite similar between plants.



CP: centrifugal pump
D: turbine drainages
N: injection nozzles
T:turbine
S1: cyclone separator
S2: van type demister
A: Atmospheric separator

Figure 1: The scrubbing plant schematic structure

The efficiencies of each section have been evaluated experimentally and by modeling by Paglianti and Sabatelli[iii] and a direct correlation between theoretical and experimental efficiencies has been pointed out. This result can be very useful in the valuation of the expected efficiencies for the total process of new and existing plants.

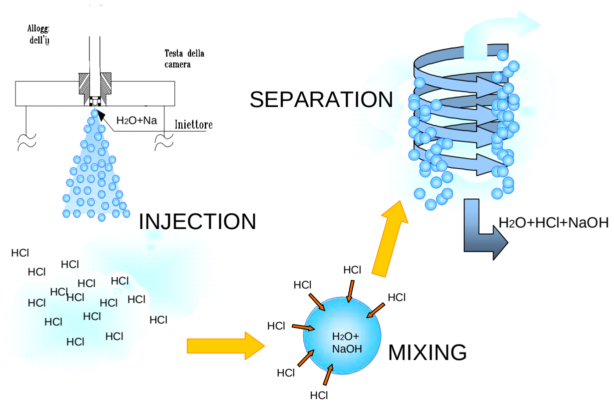


Figure 2: The scrubbing process for Chloride abatement plants

Nevertheless plant efficiencies are systematically checked by steam sampling in the main plant streams. The plant control are focused on chloride measurements upstream and downstream in the scrubbing plant with also evaluation of drifted water in the pipelines by Na concentration measurement. Another important parameter is water exhaust salinity and pH and all the secondary parameters necessary for a configuration assessment of the plant (T, P, boric acid concentration etc.). In particular pH of exhaust water measurements are necessary to check the amount of NaOH used for abatement. The amount of the latter depending on chloride concentration and well configuration on the steam pipeline that can change in time.

3. WHY THE pH MEASUREMENT

The pH measurement is performed at the water discharge of main cyclone separator in order to verify the neutralization of the solution produced in the scrubbing process. The presence of small Sodium Hydroxide excess prevents corrosion in cyclone separator, in the discharge line and also mitigates the corrosion effects in the pipeline carrying the scrubbing solution and steam before separator .

Moreover the NaOH dosed depends on chloride content that can fluctuate according natural trends or well configuration. For this reason the amounts of soda must be regulated besides the technological reasons above mentioned also for economic optimization of the abatement plant. In this case pH measurement is the main indicator to regulate soda consumptions. Water discharge pH values are also useful to verify the right functioning of the soda pumping system revealed by pH drops in case of pumping station failure.

Continuous pH measurements are a difficult task for the severe chemical-physical conditions in which the parameter is measured. High temperatures, salinity, presence of solid suspensions in the water stream and presence of hydrogen sulphide made somewhat difficult direct measurements on water discharge. Among all the high hydrogen sulphide concentrations have been proved to be the main problem on direct measurement due to interference effects on this chemical species on the reference electrodes. The solution we have found was to reduce temperature effects on pH probes and to overcome the hydrogen sulphide reference Redox potential drifts.

4. THE CONTINUOUS pH MEASUREMENT ASSEMBLY

The pH measurement assembly installed in some steam scrubbing plants has been built in order to reduce three main problems encountered in direct pH measurements:

1. High fluid temperatures reducing the electrode lifetime
2. Presence of solid particles in the discharged water with mechanical damages on electrode body
3. Presence of hydrogen sulphide affecting reference electrodes with electric potential drifts along time and consequent non accurate pH measurements.

Every electrode has a natural aging. High temperatures accelerate the process reducing normal lifetimes from 2-3 years to few months in high temperature environments. In order to overcome this problem that required high maintenance costs we have adopted a cooling system in our equipment in order to obtain liquid temperatures allowing long electrode durations..

The mechanical damages to electrodes due to particles presence have been reduced by continuous drawing of small flow rates (0.2-1 l/min) of the exhaust solution from discharge piping and then cooling before contact with electrode. Particles are also decanted in calm chamber before reaching the electrode.

The interference of hydrogen sulphide due to reactions at the reference electrodes has been overcame by separating the measurement electrode of glass-type from reference electrode of Ag/AgCl type with a saline junction and keeping the reference in a separate reference solution. This has allowed the prevention of the following reference electrode reaction:

$$2Ag+ + HS^{-} + OH- \rightarrow Ag_2S + H_2O \qquad [1]$$

that gives unstable measurements and also electrode breaking down.

The assembly is shown in Fig. 3, 4.

Figure 3: The cooling section on the left and the intermediate recipient for particles decantation and removal

Figure 4: The entire assembly is visible. Starting from the upper left side of the picture we can see the reference electrode holder (A), the measurement electrode holder (B), the calm chamber (C) and the cooling section (D)

Another positive feature is room pressure measurement that prevents further contamination at the electrode junctions.

5. FINAL CONSIDERATIONS

The continuous pH measurement assembly adopted in some steam scrubbing plants has revealed to be reliable system for plant control, plant failure alerting and also for Sodium Hydroxide consumption control. The system requires poor maintenance and long time intervals between calibration. This feature allows to perform maintenance during routine chemical-physical plant controls without further personnel involvement. Low construction costs and a simplified layout make the assembly suitable to be implemented in existing plants. Five assemblies are currently running in major steam scrubbing plants and a total continuous pH measurement equipment implementation program is currently in progress.

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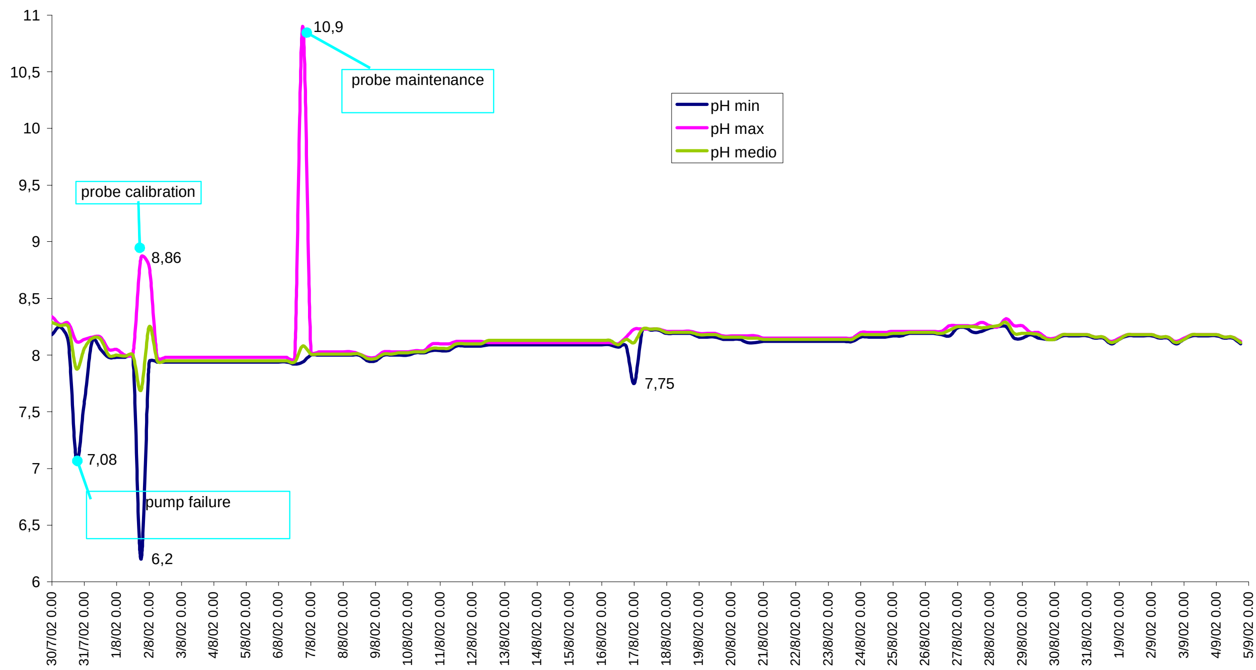

Figure 5: An example of data collected with 6 hour averaging. Several events can be pointed out (spikes in graph): sodium hydroxide pump failure, calibration, maintenance. The other features are dependent on steam quality fluctuations

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[i] "Erosion and corrosion problems experienced during the operation of geothermal turbines in Italy". Bracaloni, M., Culivicchi, G., and Fornari B. (1995). *Proc. World Geothermal Congress* 1995, Vol. 4, pp. 2427 – 2432.

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