

ABATEMENT OF HYDROGEN CHLORIDE IN GEOTHERMAL POWER PLANTS

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Keywords: Corrosion, HCl, Abatement**ABSTRACT**

Corrosion mitigation through the abatement of hydrogen chloride is one of the most important operations that must be carried out in some geothermal power plants. When chloride concentrations in the steam are higher than a few ppm_w, scrubbing of the steam is necessary to prevent corrosion of the gathering system and failure of the turbine blades.

In the Larderello area, this operation is usually performed through direct injection of a caustic solution in the steam pipeline immediately upstream from the power plants. In the last few years, static mixers have been used to reduce the length of pipeline necessary for the steam scrubbing to take place.

In this paper, some simplified models are proposed for the calculation of the chloride abatement process in pipelines, static mixers, centrifugal separators and vane type demisters.

The results obtained from these models are compared with the field data gathered from power plants operating in the Larderello area.

1. INTRODUCTION

Geothermal steam containing volatile chloride has been reported in steam fields throughout the world, such as Larderello (Italy), Tatum (Taiwan), Krafla (Iceland), St. Lucia (Windward Islands) and The Geysers (USA) (Hirtz *et al.*, 1990).

Most geothermal researchers agree that volatile chloride in geothermal steam is transported as HCl. However, there is a considerable debate over the device of HCl generation: possible mechanisms are the complete evaporation of NaCl solutions at high temperature, volatility of HCl in high temperature saline brines and mineral-halite reactions (Hirtz *et al.*, 1990).

The presence of HCl in superheated steam and subsequent corrosion has proved to be one of the major operating problems (Allegrini and Benvenuti, 1970). Corrosion is believed to be related to the partitioning of HCl into any liquid present and the subsequent dissociation into Cl⁻ and H⁺.

Carbon steel steam pipelines have a satisfactory life span when the chloride content is nil: general corrosion is slow and evenly distributed, forming wide, irregular pits and blisters in the points most affected by the formation of condensate. In the presence of chlorides, corrosion is still negligible above the dew point, but a fast pitting corrosion occurs in points where condensation takes place, as acid solutions are formed that may rapidly lead to localized failures of the pipe. Since the steam is normally superheated at the wellhead, a proper design and good thermal insulation could prevent condensation and thus

corrosion. Of course, crossing of the steam saturation line cannot be avoided in the turbines.

In power plants fed by steam with a chloride content roughly over 5-10 ppm_w, corrosion phenomena on the blades of the stages where this transition occurs give rise to serious operating problems. The typical blade failures are originated by stress corrosion cracking, with cracks starting at the bottom of a pit and propagated by corrosion fatigue up to the final mechanical break. The formation of acid chloride condensate in some geothermal fields resulted in failures of steam line components, causing frequent outages and curtailments of these plants (Allegrini and Benvenuti, 1970). Also the exfoliated corrosion products have had a strong impact on plant equipment by plugging steam strainers and eroding turbine blades.

In Larderello, an intensely exploited vapor-dominated geothermal field in Tuscany (Italy), hydrogen chloride was seldom detected in the steam before 1960. After 1970, HCl concentration increased rapidly up to 80 ppm_w in the central area of the field and up to 10 ppm_w in other areas; chloride content peaked during 1975-1980 and then decreased in response to the beginning of condensate reinjection. Recent data from deep wells drilled in peripheral areas of the field show high chloride concentrations.

2. DEVELOPMENT OF STEAM SCRUBBING SYSTEMS

The practice of steam scrubbing goes far back in time: when the first discharging-to-atmosphere turbines were installed in Larderello, it was used on the exhaust steam for boric acid recovery by injecting a stream of condensed water.

Since the introduction of the direct steam condensing cycle in 1950, steam scrubbing upstream from the power plant has been performed. The first configuration used consisted of steam scrubbing performed in a countercurrent column equipped with eight special plates, six for steam-water contacting and the upper two for entrained droplet separation. In the second configuration simpler equipment was used, consisting of water sprayers and an axial centrifugal separator located along the steam pipeline some tens of metres downstream from the injection point.

After the abandonment of boric acid recovery, scrubbing plants with a similar scheme were installed upstream from the power plants in order to avoid corrosion damage to turbine blades when the chloride content of the steam exceeded 5-10 ppm_w. An alkali solution was injected, instead of water, in order to avoid corrosion problems in the steam pipeline and separators.

Tests were conducted to evaluate the performance of the

hydrogen chloride scrubbing systems and to determine optimum operational parameters: it was found that HCl abatement efficiency first increased with the injected liquid flow, then remained constant. The NaOH concentration in the injected water was adjusted to obtain a separated liquid flow with a pH ranging between 7.5 and 8.5. The practice of NaOH addition to the injected water is aimed at preventing corrosion problems on the steam pipeline downstream from the washing solution inlet point since it does not produce a significant increase in HCl abatement.

The standard chloride scrubbing system for a modular 20 MW unit consists of injection nozzles located about 50 m upstream from the separator and a vane type demister located before the turbine inlet. The typical operating conditions for such plants (treating 110 t/h of steam) were adjusted by varying the injection rate of alkali solution and its concentration (1-2 g/l) so as to obtain a separated liquid flow rate of 2.5-3.5 t/h with a pH ranging between 7.5 and 8.5.

Similar steam scrubbing systems have been successful in reducing corrosion to acceptable levels at The Geysers field (Bell, 1989; Hirtz *et al.*, 1990) and at Coldwater Creek steam field (Meeker and Haizlip, 1990). At Coldwater Creek, a dual steam scrubbing station has been designed to desuperheat steam, neutralize pH and remove a liquid containing Cl^- ; water mixed with a 25% solution of NaOH is injected downstream from each well through atomizing nozzles and then separated by means of a vertical cyclone separator installed approximately 75 m from the injection pools.

Two stage injection (upstream with deoxygenated condensate and downstream with dilute caustic solutions) was also proposed for The Geysers. Atomizing a caustic solution into superheated steam may cause the deposition of caustic on the piping surface before saturation occurs, causing serious corrosion or caustic embrittlement; two cyclones are provided for series or parallel flow.

In order to eliminate the operating problems still affecting scrubbing systems at Larderello field, their design has been modified and field tested in the last few years.

Some circuits have been modified both to improve the separation, by reducing the quantity of liquid entrained downstream from the separators (cyclones are inserted upstream from the vane type demisters), and to reduce the length of the pipeline, subject to corrosion and scaling, between spray and separators. As it was not possible to reduce the length of the pipe without a remarkable reduction in chloride abatement efficiency, a static mixer was selected as a contacting device between the steam and the scrubbing solution. A brief description of the evolution of the examined power plants follows.

The scrubbing system of the S.Martino 2 (SM2) plant (Fig.1) has undergone several modifications. The first configuration allowed for the use of sprays placed 50 metres from a vane type demister; then, because of problems involving excessive entrainment, a cyclone was inserted between the sprays and the vane type demister. Finally, in order to reduce the length of the pipeline, the sprays were moved to a distance of 5 metres from the cyclone, and a static mixer was inserted between these two elements.

The S.Martino 3 (SM3) plant is equipped with a washing system that makes it possible to evaluate the pipeline's influence on HCl abatement. Two different configurations that allow a distance of 5 or 50 metres between the sprays and the vane type demister can be chosen.

The Cornia 1 (CO1) plant has a particularly complex geometry since there are two steam ducts (VC8 and Puntone) which feed the plant. The abatement system consists of sprays placed in each pipeline, approximately 40 metres from the junction of the two steam ducts, a vane type demister is located downstream from this point. Recently the system was modified by inserting a static mixer and a cyclone in each pipeline with a distance of 5 metres between the two.

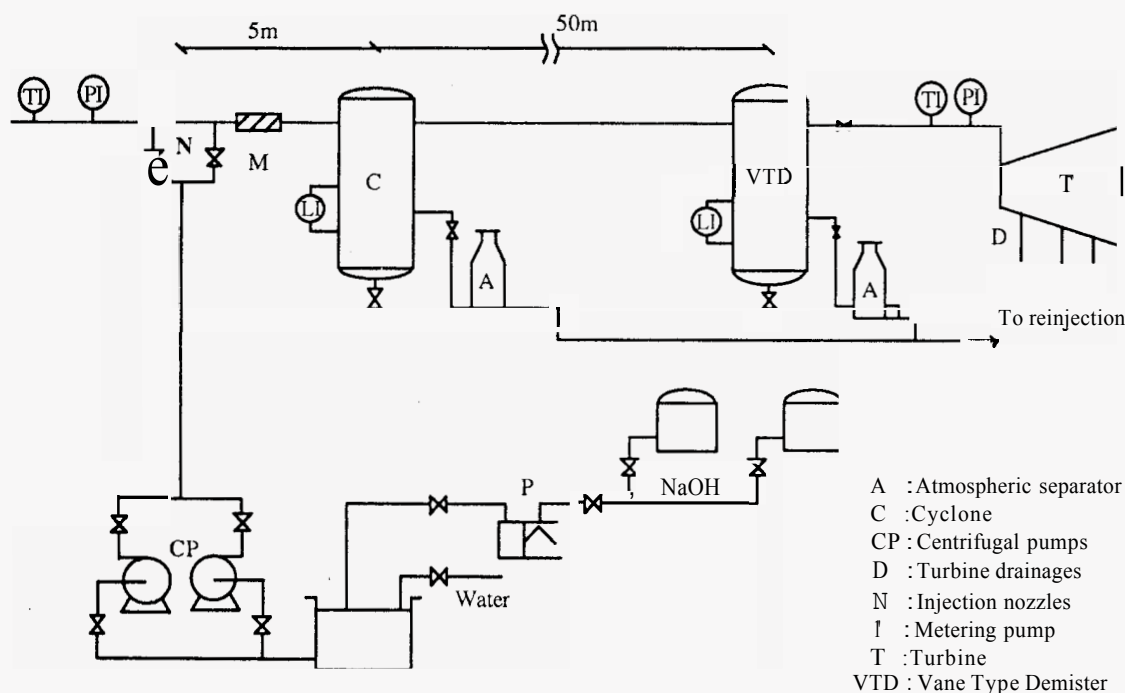


Fig. 1: Schematic design of S.Martino 2 corrosion mitigation system

Serrazzano (SER) is the last plant analyzed. In 1990 this plant was equipped with a scrubbing system which allows a certain degree of operational flexibility: the central collector branches out into two pipelines, each having two separators in series (cyclone and vane type demister in that order). The injection of soda can be carried out either on the central collector, approximately 60 metres upstream from the cyclones, or in each branch, 9 metres upstream from the cyclones. This configuration, permitting the use of one or both of the branches and two washing solution injection sections, makes it possible to evaluate the importance of steam velocity and distance between sprays and separators.

Table 1 gives a brief summary of the characteristics of the analyzed power plants.

Plant	T (°C)	P (bar)	Pipe diameter (m)	Steam (t/h)	Washing liquid (t/h)
SM3	200	11	0.56	110	8-10
SM2	200	11	0.56	110	8-10
CO1	162	6.5	0.45	40+70	5+7
SER	180	7	0.56	110	12

Table 1

Before proceeding with the schematic description followed during the analysis of the scrubbing plants, it is necessary to point out some problems in interpreting the analytical data. Since the steam incoming the abatement system is generally superheated, the analysis of the Cl^- content is not particularly complex. However, the analysis of the washed steam, which can contain small drops of liquid, is more complicated. As the Na^+ ions are absent in the steam coming from the well, their presence in the steam downstream from the washing is an indicator of the amount of liquid entrained in the steam. Any Na^+ ions are due to the presence of NaOH or NaCl. This uncertainty is therefore reflected in the analysis of the data related to the HCl abatement: if the Na^+ is ascribable only to the NaCl, the chloride ions present downstream from the washing section are in some degree due to the presence of HCl and also to the presence of NaCl. Otherwise, if the Na^+ is attributed only to the presence of NaOH the Cl^- is entirely due to the HCl which has not been adsorbed.

A further indication of the quantity of liquid entrainment is given by analysis of the liquid from the first drainage of the turbine.

3. ANALYSIS OF THE ABATEMENT SYSTEM

In the schematic description proposed for the scrubbing system analysis, the plant is subdivided into units and in each one correlations are found for the calculation of the surface and the gas phase mass transfer coefficient. The analysis carried out does not take into account the resistance to mass transfer in the liquid phase, because the HCl abatement in caustic solutions belongs to the class of absorption with instantaneous chemical reaction. HCl and NaOH concentrations fulfil the condition proposed by Astarita (1967) and allow us to affirm that the reaction surface coincides with the liquid-gas interface (Surface Reaction Regime), therefore the resistance to mass transfer is concentrated

in the gas phase. The washing units into which each scrubbing circuit is subdivided are: spray, static mixer, pipeline and liquid-steam separator.

In this work the abatement in the first section, contained between the section in which the sprays are located and the mixer section, if there is one, is schematized as due to the presence of small drops of liquid dispersed in the steam phase. In the next section, given the mechanical analogy between static mixers and structured packings, a scheme like the one proposed by Bravo *et al.* (1991) for columns equipped with structured packings, was assumed. Finally, for the section of pipeline downstream from the mixer, it is possible to assume that an annular flow regime is established. In this case the HCl abatement will be due both to the film of liquid which flows on the wall and to the drops dispersed in the steam phase. In the configurations where a static mixer is absent, there is no immediate solution to the problem of distinguishing between the section of pipeline where the abatement is due to the presence of drops generated by the spray, and the pipeline where the abatement is due to drops generated by the annular flow. The length of the segment of influence of the spray is estimated as the distance at which the last drops produced deposit again on the wetted wall. In the following unit the spray contribution is considered nil and the pipeline is analyzed estimating both the quantity of liquid in the film and the number and size of the drops carried by the steam.

From this preliminary analysis the coexistence of two variables emerges: one relative to the film, easy to evaluate, and one relative to the drops, much more complex to identify as it depends on the conditions of superficial velocity of both the steam and the liquid, as well as geometric characteristics.

The analysis proposed in this paper allows us to evaluate the contribution to the HCl abatement of each unit and the results agree with the experimental data.

For each unit, it is possible, through a mass balance between the inlet and outlet sections, to define an abatement capacity as:

$$\frac{C_{OUT}}{C_{IN}} = \exp \left[-\frac{K_g \cdot A}{V} \right] \quad (1)$$

where C_{IN} and C_{OUT} are the concentrations of HCl in the steam at the inlet and outlet sections respectively (mg/m^3), V is the volumetric steam flowrate (m^3/s) and A and K_g are the area (m^2) and the gas phase mass transfer coefficient (m/s) calculated for this specific case. Let us examine in more detail the behavior of the units identified.

Spray: The introduction of the alkaline solution in the steam pipeline is a critical aspect of the washing processes of geothermal plants. The problem of their corrosion, scaling and subsequent replacement makes the choice of material, positioning and, above all, type a matter for careful study. The operation of the nozzles also contributes to the washing of the steam in terms of the area produced. Once the construction characteristics and the operational conditions of the sprays are known, the mean size and the quantity of the drops produced can be estimated, as well as the trajectory that these follow in the steam pipeline. In this way it is possible to define area and gas phase coefficient for the mass transfer.

The proposed analysis is based on the simplified hypothesis that the sprays produce drops having identical diameter with

uniform distribution with respect to the angular dispersion, and that the drops, once formed, are not subjected to further subdivisions.

The generic drop produced by the spray is followed in its trajectory from the nozzle exit (with an initial velocity calculated on the basis of the liquid flow rate and the spray section and with an angle of incidence with respect to the pipeline which varies according to the type of nozzle between 0 and 60°) to the instant it impacts the pipe surface or reaches the stem velocity (in the case of a spray positioned in front of a mixer a further condition, represented by arrival at the mixer, is introduced).

The motion is determined on the basis of the equilibrium of the inertial, frictional and gravity forces. For each drop the velocity can be defined for successive positions, hence its Reynolds number (Re_D); from the Reynolds number the mass transfer coefficient Kg_D (m/s) is computed:

$$\frac{Kg_D \cdot d_D}{D_V} = 2 + 0.738 \cdot Re_D^{0.5} \cdot Sc^{0.33} \quad (2)$$

where d_D (m) is the drop diameter, D_V (m²/s) the HCl diffusion in the steam and Sc is the Schmidt number related to the steam phase.

Based on the local value of Kg_D it is possible to define an average mass transfer coefficient Kg (m/s) related to the whole spray unit. Knowing the number and the surface area of the drops produced by the spray, the spray abatement efficiency can be calculated by equation (1).

Mixer: Recently, in some plants, a configuration which allows for the insertion of mixing units on either a vertical (S.Martino 2) or horizontal (Cornia 1) section of pipeline has been adopted. These mixers have been installed at a distance of 0.5 metres from the sprays and approximately 3-4 metres from the cyclones. The introduction of the mixing unit increases the exchange surface and the relative velocity between the phases, thus improving the abatement efficiency. Further, the presence of the mixer causes turbulence in the outgoing steam, which increases its exchange capacity. Data and correlations describing the two effects that we expect from the mixer are not available in literature. However, for the mass transfer one can refer to the structured packings of analogous geometry to that of the static mixers. Hence Bravo *et al.* (1991) defined the mass transfer Coefficient Kg_M (m/s) as:

$$\frac{Kg_M \cdot d_E}{D_V} = 0.054 \cdot Sc^{0.33} \cdot \left(\frac{U_E \cdot d_E \cdot \rho_V}{\mu_V} \right)^{0.8} \quad (3)$$

where d_E (m) represents the equivalent diameter of each channel formed by the sheets which make up the mixer, U_E the effective velocity of the steam (m/s) and ρ_V (kg/m³) and μ_V (kg/m/s) the density and viscosity of the steam respectively.

The specific wetted area a_E (m²/m³), that is, the effective surface that participates in the mass transfer, can be calculated by again referring to the structured packings (Bravo *et al.*, 1991). The term $Kg \cdot A$ for the mixer is:

$$Kg \cdot A = Kg_M \cdot L_M \cdot \frac{\pi}{4} \cdot DC^2 \cdot (a_E + 4 / DC) \quad (4)$$

where L_M (m) is the total length of the elements making up the mixer and DC (m) the diameter of the pipe whose walls are assumed to be wet. The procedure illustrated above, permits calculation of the amount of HCl abated under the hypothesis that

the washing fluid flows as a film wetting the sheets which make up the mixer. This assumption is certainly cautious, as the contribution of any drops of liquid transported by the steam phase is neglected; another cautious assumption is to neglect the turbulence caused by the mixer, which certainly produces an increase of the mass transfer coefficient in the pipeline downstream from the mixer

Pipeline: The flow configuration of a mixture of gas and liquid in a pipeline depends on the velocity of the two phases, their physical properties and the geometry of the pipeline. In the case of the examined geothermal plants the superficial velocity of steam and liquid is approximately 25 and 0.0001 m/s respectively, hence the assumption that in the pipeline an annular flow regime exists, characterized by the presence of a liquid film which flows along the pipe wall, and a steam flow, with drops dispersed in it, moving in the center of the pipeline. Under these conditions a slip velocity is developed between steam and washing liquid, which produces a mass transfer between the two phases. In order to evaluate the contribution of the "pipe" element to the mass transfer it is necessary to estimate the distribution of the washing liquid between film on the walls and drops. Annular flow in horizontal pipelines has been studied in quite a systematic way for the last ten years, and in the literature it is possible to find correlations for calculating the parameters we need: Laurinat *et al.* (1984) supply a correlation for the calculation of the liquid fraction entrained as droplets in the steam.

The surface film contribution to the washing of the stem can be evaluated referring to the behavior of a "wetted-wall column". For the pipeline, the mass transfer coefficient Kg_T (m/s) is based on Johnstone and Pigford's equation (1942) for turbulent flow of gas in a perfectly smooth pipeline. This is modified for rough pipelines as proposed by Nunner (1956) for the calculation of heat transfer coefficients and the mass transfer coefficient is increased by a factor (f_l/f_s) where f_l is the friction factor at the interface, while f_s is the one calculated for perfectly smooth pipelines. The resulting equation is:

$$\frac{Kg_T \cdot DC}{D_V} = 0.023 \cdot \left(\frac{f_l}{f_s} \right) \cdot Sc^{0.4} \cdot \left(\frac{U_V \cdot DC \cdot \rho_V}{\mu_V} \right)^{0.8} \quad (5)$$

Laurinat *et al.* (1984), like Aziz and Govier previously (1972), observed that, for any value of the liquid flow rate, the fraction f_l/f_s has an asymptotic limit of 2.3 for high Reynolds numbers which can be attributed to the permanence of surface film even at high velocities.

For the drops entrained in the steam, the work of McCoy and Hanratty (1977) allows us to calculate (on the basis of the steam and liquid velocity, the "entrainment" fraction and the pipe dimensions) the number and characteristics of the drops produced by the annular flow.

The motion of the single drop can be followed from the moment it is produced by the film to when it is deposited back on the film. It is possible, for fully developed conditions, to know the number of drops dispersed and their velocity path. The integration of the motion shows that only a small part of the drops has a speed different from that of the gas, which permits us to simplify the estimate of the washing Contribution supplied by the drops, assuming that they all have the same velocity as the steam. Referring to equation (1), and unifying the contributions of the wall film and dispersed drops, it is possible to write:

$$Kg \cdot A = L_T \cdot (N_T \cdot a_p \cdot Kg_p / U_V + Kg_T \cdot \pi \cdot DC) \quad (6)$$

where L_T (m) indicates the pipeline length, N_T the number of drops which flow in the pipeline, which is defined on the basis of the amount of liquid entrained in the steam phase (Laurinat *et al.*, 1984) and their diameter (McCoy and Ilanratty, 1977), to which is associated a surface a_p and an exchange coefficient Kg_p (m/s) calculated with (2) after substituting d_D with d_m , the mean dimension of the drops (Sauter mean diameter, Ambrosini *et al.*, 1991).

Drop-steam separators: The liquid-steam separators installed in the ENEL plants are vane type demisters or cyclones; our aim is to estimate the contribution to the abatement of the HCl present in geothermal steam for each one of these.

The simplified approach suggested in this paper is to calculate the surface of the mass transfer considering only the wet surface of the separators and neglecting the contribution due to the presence of drops. This is a cautious approach, but it is simple and makes the system analysis easier.

The vane type demister has been installed ever since the first washing systems were installed to separate the liquid from the steam. Verlaan (1991) proposed correlations for evaluating the diameter of the drop separated with 100% efficiency as a function of pack geometry and steam characteristics (velocity, density, viscosity).

This value, compared with the distribution curve of the drops in the pipeline with annular flow (Tattersson *et al.*, 1977), permits evaluation of the number of curves necessary to eliminate the drops entrained in the steam, and therefore estimation of the wet surface of the pack (A_{VTD}). The term Kg_{VTD} (m/s) is calculated with equation (5), modifying the channel diameter and the gas velocity on the basis of the geometric characteristics of the pack.

The "wetted wall column" scheme can still be used for the cyclones. Knowing the geometry of the separators the wet area is identified (A_{CY}). As for the motion of the steam, the velocity which has to be introduced in the calculation of the coefficient Kg_{CY} , is the resultant of the axial and tangential components.

4. RESULTS AND CONCLUSIONS

By following the scrubbing system from the spray to the separator, through all the different washing units, it is possible to calculate the abatement efficiency and compare it with the field data of the various configurations examined.

To check if this model works it would be better to measure the efficiency of each component of the washing loop. Unfortunately, due to the fact that the results produced in this work derive from working power plants, HCl concentration is measured only in the steam entering and leaving the washing loop. Only a few data collected at S.Martino 2 which give the HCl concentration also downstream from the mixer are available; in this case the HCl concentration expected from the model agrees with the experimental values.

The global efficiency values relative to the analyzed plants are shown in Fig. 2; the experimental data have been reported as a mean value of 5-7 different measurements. The agreement between the values predicted by this paper and the experimental data obtained for all the configurations examined can be easily seen.

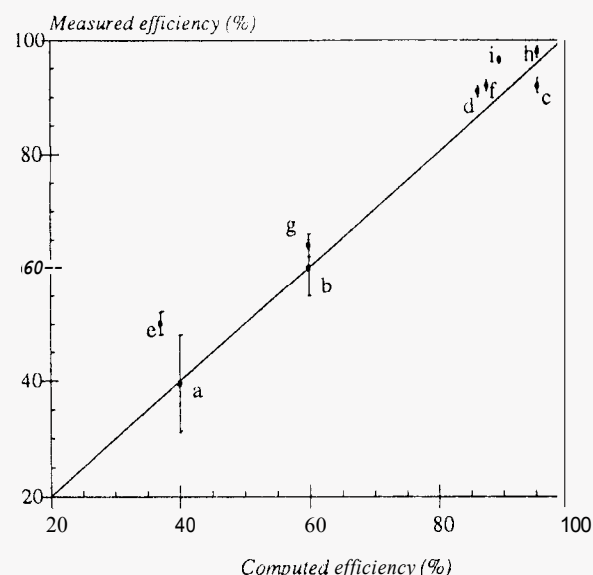


Fig.2 Comparison between calculated and measured scrubbing efficiency at Larderello steam field

(a) Serrazzano, spray from 9 m-only one branch-cyclone; (h) Serrazzano, two parallel branches-spray from 9 m-cyclone; (c) Serrazzano, parallel branches-spray from 60 m -cyclone; (d) S.Martino3, spray from 50 m-vane type demister. (e) S.Martino3, spray from 5m-vane type demister; (f) S.Martino2, spray from 50 m-vane type demister; (g) S.Martino2, spray-mixer-5 m of pipe-cyclone; (h) Cornia 1, spray from 40 m-vane type demister, (i) Cornia 1, spray-mixer-5 m of pipe-cyclone-vane type demister.

Some clarifications seem to be necessary. In Fig.2 the efficiency of Cornia 1 (h) exceeds the efficiency measured at S.Martino 3 (d), which has a similar washing system. This anomaly can be explained by the fact that the cyclone settled at Cornia 1 presents a lower abatement efficiency so the pipeline between the cyclone and the vane type demister is wetted and for this reason supplies a further exchange surface to the HCl abatement. Another anomaly is the lower abatement efficiency of S.Martino 2 (f) with respect to Cornia 1 (h) and of Serrazzano (a) with respect to Serrazzano (b) although the longer pipelines. These apparent contradictions are due to the different configurations of the analyzed plants: both Cornia 1 (h) and Serrazzano (b) have a double steam pipeline as against the single pipeline used in S.Martino 2 and Serrazzano (a); the double pipeline increases the available surface per unit length. The last case that needs clarification is the comparison between S.Martino 3 (e) and S.Martino 2 (g). These washing systems have the same length of pipeline but S.Martino 2 has the highest HCl abatement efficiency due to the presence of the mixer and the cyclone, which increase the surface available for the mass transfer.

Fig.3 shows the calculated abatement efficiency of each unit of the S.Martino 2 present configuration. It is possible to conclude that the relative abatement efficiencies of the single units are: 13% for the spray, 37% for 1.2 m of static mixer, 32% for 5 m of pipeline and 18% for the cyclone.

The proposed mathematical procedure allows good evaluation of the contribution of each unit in the abatement system and can thus be used to optimize plant design in order to maximize HCl abatement.

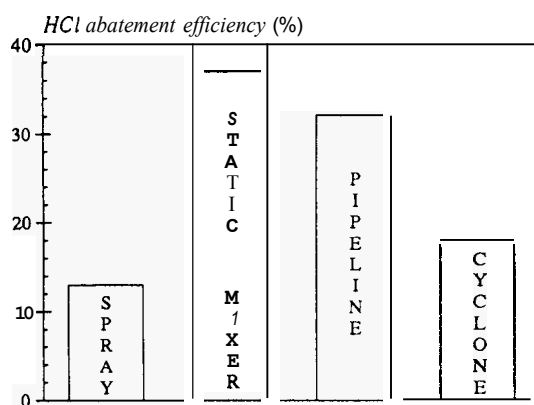


Fig.3 S.Martino 2 abatement efficiency

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