

Metallic Contaminants Generation from Tubing during Start-up and Following Moisture Upsets in HCl Distribution Systems

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Contamination control has always been an important issue for IC manufacturing processes. Within the area of corrosive gas distribution, metallic contamination is a constant threat to process yield. This paper focuses on metallic contamination resulting from low pressure HCl gas flow through tubing materials during system start-up and following exposure to moisture. The paper discusses the effect of HCl exposure on two tubing materials. Data relating to the type, physical state, and concentration of metallic contamination is included. Surface chemistry mechanisms are proposed in relation to the observed phenomena. The comparison of two tubing materials permits performance, cost and design implications to be considered.

INTRODUCTION

As device size continues to shrink, the influence of contamination grows in importance. The typical approach in minimising contamination related to gas supply, is to increase the purity specifications of gases at the point of use. It is generally accepted that gas purity must increase by a factor of 10 for each technology level size decrease [1]. Consequently, gas suppliers, equipment manufacturers, piping specialists, and those responsible for contamination control need to extend their knowledge of gas behaviour in distribution systems. In inert gas distribution systems, e.g. N_2 , moisture is considered by many as a predominant contaminant and has been analysed extensively in the past [2]. These systems are generally well understood and computer models exist which accurately predict their behaviour [3].

The area of corrosive gas behaviour within a piping system is more challenging because of the additional surface chemistries and reactions that affect the piping surface structure, leading to the generation of metallic contaminants. This corrosion can lead to the premature failure of sensitive gas system components, such as mass flow controllers and pressure regulators, leading to costly repairs and even costlier down-time. Moisture in reactive gases enhances corrosion of piping materials. In previous research, BOC and IMEC have focused on moisture transport in HCl gas distribution systems [4]. Relatively little is known, however, about volatile (gas phase) metallic contaminants which can be produced from corrosive gas interactions with metal surfaces.

This paper focuses on metallic contamination resulting from HCl gas flow through tubing materials during system start-up and following exposure to moisture. These moisture upsets simulate the effect of moisture introduction to the system, representative of an improper cylinder change-over procedure resulting in an ingress of moisture, or inadequate purging resulting in moisture outgassing when HCl is introduced [5]. HCl was selected as the typical corrosive gas due to its widespread use in plasma etching and thermal oxidation processes.

EXPERIMENTAL

The experimental rig shown in figure 1, was designed and constructed to enable metallic contaminants to be counted and captured during dynamic process conditions, illustrative of those experienced in fab gas lines at the point of use. Low pressure conditions permit Joule-Thomson effects to be eliminated. J-T effects are normally experienced following expansion from a high pressure to a lower one resulting in liquid condensation and enhanced corrosion.

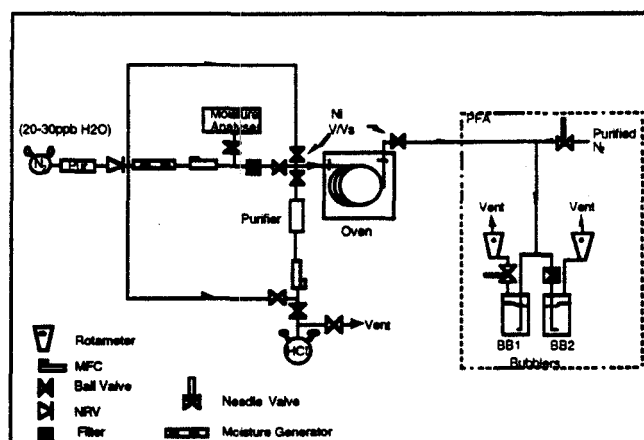


Figure 1. Schematic of experimental rig

The rig configuration permitted mixtures of purified HCl and N_2 mixed with calibrated H_2O concentrations, to flow through the test material, which was maintained at a controlled temperature of 25 °C. All upstream peripheral tubing consists of EP-SS up to the point where the two streams meet. Parts wetted by moist HCl are made of Ni-

200 or PFA to minimise system contributions to the measurements. The gas exiting the test piece is scrubbed in two quartz bubblers. Data on the metallic content of the gas flow is obtained using TXRF (Atomika 8010) to analyse microsamples of the bubblers' solutions dried on Si wafers. The TXRF limit of detection is $\sim 10^{11}$ atoms/cm². The actual detection limit for gaseous concentrations depends on gas flow rate and time as well as bubbler and sample volumes, resulting in a dependency on flow time as shown in Fig. 2.

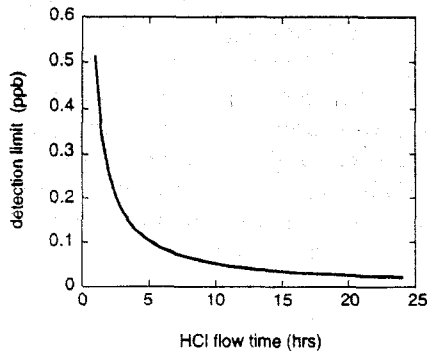


Figure 2. Limit of detection for metals in HCl gas flow as a function of flow time.

By installing a 0.003 μm in-line particle filter (Millipore Wafgard GT Plus, PTFE membrane in PFA housing) upstream of one of the two bubblers, differentiation between total contaminants and small contaminants, i.e. small particles ($< 0.003 \mu\text{m}$) and/or volatiles, is possible. The filter used is of a similar specification to those installed in fabs at POU, the principal difference being that it is non-metallic to prevent background interference.

In this paper, results are presented for the corrosion of the two predominant fab piping materials, 316L EP-SS and Hastelloy C-22. The tubes are 6m in length and coiled to a diameter of 10". Each tube has VCR connectors of the same material welded to each end and are cleaned with acetone and DIW and baked for 24 hours at 150 °C prior to HCl exposure. The experiments are performed at a pressure slightly above 1 atm under a total flow of 0.2 SLM. This flow is either purified HCl (Millipore Waferpure WPRV 200SC, < 100 ppb H₂O), simulating normal flow conditions, or 'moist' HCl, a 50/50 mixture of HCl and moist N₂ giving 10 ppm moisture in HCl. The moist HCl is admitted for periods of 1 to 3 hours to simulate moisture ingress into a distribution system.

RESULTS

The main contaminants generated during the exposures of both EP-SS and C-22, are Fe, Ni and Zn. Trace amounts of Cu and Cr were also observed but not in sufficient quantities to enable trends to be viewed. Tables 1 and 2

highlight the average contaminant concentration (volumetric) in HCl during the initial exposure of the test materials.

Material	Average concentration (ppb)		
	Fe	Ni	Zn
EP-SS	1.02 ± 0.26	0.19 ± 0.05	0.12 ± 0.03
C-22	0.46 ± 0.17	0.08 ± 0.03	0.10 ± 0.03

Table 1. Average total contaminant concentrations in HCl during initial 48 hour exposure to purified HCl (± 3 Std. dev.).

Material	Average concentration (ppb)		
	Fe	Ni	Zn
EP-SS	1.02 ± 0.14	0.14 ± 0.03	0.16 ± 0.03
C-22	0.48 ± 0.09	0.06 ± 0.05	0.06 ± 0.02

Table 2. Average small contaminant concentrations in HCl during initial 48 hour exposure to purified HCl (± 3 Std. dev.).

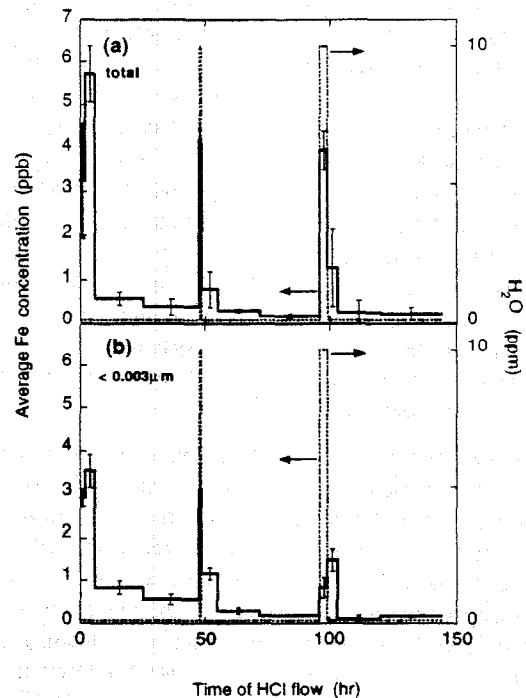


Figure 3. Average Fe concentration in HCl flowing through EP-SS tubing, following exposure to purified and moist HCl (± 3 Std. dev.). (a) total contamination, (b) small contaminants.

Upon comparing the TXRF data in relation to the experimental time, Figures 3 and 4, clear trends emerge. During initial exposure the contamination levels rise over the initial 6 hour period and then decrease. Upon exposure to moist HCl for 1 hour the trend is repeated. A subsequent 3 hour exposure shows a further repetition of the trend. Similar trends were observed for Ni and Zn in both EP-SS and C-22 tubing.

Contaminants are generated as both large particles and small contaminants.

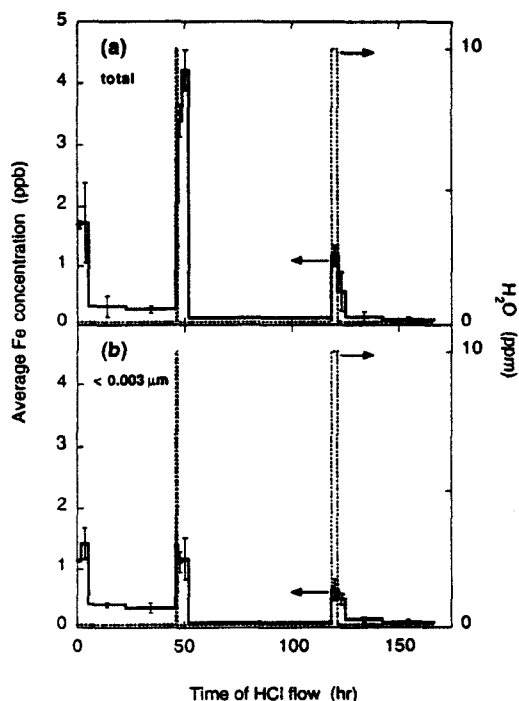


Figure 4. Average Fe concentration in HCl flowing through C-22 tubing, following exposure to purified and moist HCl (± 3 Std. dev). (a) total contamination, (b) small contaminants.

DISCUSSION

Contaminant Generation

For each of the tubing materials, Fe was identified as the predominant metallic contaminant. Quantities of Ni and Zn were also identified along with trace amounts of Cr and Cu. With the exception of Zn, each of identified metals can be found in C-22 and EP-SS tubing. Background interference was accounted for and confidence regarding the non-contribution from the Ni parts was high given the fact that

Ti was not detected as with previous work which included Ni tubings [4][6].

To understand the contaminant generation associated with initial exposure of the tubing material to HCl, as illustrated in Figures 3 and 4, the surface chemistries have to be considered. It is thermodynamically possible for HCl to react with the tube surface oxides at room temperature to form metal chlorides. For example



Similar equations can be derived to demonstrate that metal chlorides can also be produced from reactions of the virgin metal and metal hydroxides in HCl. Upon comparing the molar volumes of the reaction products, chlorides have higher molar volumes than the oxide, e.g. Fe_2O_3 is $30.5 \text{ cm}^3/\text{mol}$, FeCl_2 is $40.1 \text{ cm}^3/\text{mol}$ and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ is $69.0 \text{ cm}^3/\text{mol}$ [7]. The volume expansion resulting from the above reactions will increase the mechanical stresses inside the surface layer causing a "flaking off" of particles. Volatiles will contaminate the gas flow as a result of the relatively high vapour pressure of the corresponding corrosion product. As HCl continues to flow, most probably a chloride layer forms on top of the oxide layer, protecting the tubing wall against further corrosion, to some extent.

Chlorides are particularly hydrophilic, forming hydrates e.g. $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$. When moisture upsets occur, the moisture is readily absorbed by the chlorinated surface. This absorption causes volume expansion, thereby increasing the mechanical stress within the surface layer with the same effects as mentioned previously.

Size Distribution

From Figure 3 and 4 it can be observed that Fe is present as both large particles and small contaminants. A significant fraction of the generated contaminants are small and pass through the filter. Upon reviewing the data for both EP-SS and C-22 tubing it is not apparent that a particular metal has a preference in forming large or small contaminants. One trend which can be seen is as the tubing stabilises the contaminants are more likely to be small.

Material Comparison

Evaluation of the data contained within Tables 1 and 2 and Figs. 3 and 4 suggests that in the case of HCl gas, Hastelloy is a slightly more resistant material generating less contaminants than EP-SS for each of the three metal contaminants observed.

CONCLUSION

The present study agrees with the findings of previous research that corrosion of 316L EP-SS and Hastelloy C-22 tubing does occur under purified HCl flow [4][6]. The

trends discussed in the previous section infer that a system can achieve a stabilised state if the purified HCl conditions are maintained following the initial exposure. However, if conditions change and moisture enters the system, more corrosion products are generated. Moisture ingress is most likely to occur during cylinder changeover or refilling of a bulk storage system. It is therefore not only imperative that those responsible for managing such tasks have correct procedures to follow but also that the connection systems are properly designed to permit adequate purging. Residual moisture lurking in a distribution system as a result of poor commissioning purge procedures will also create problems. Such moisture may reside in deadlegs, e.g. tie-in points for future lines, but will not create problems during normal flow conditions as the main flow routes have been adequately dried. However, when the system pressure drops, the deadlegs release their contents and moisture enters the mainstream lines. It is important therefore that systems are properly designed to minimise deadlegs and to permit adequate purging of the entire system. Fortunately computer model packages have been developed to help the engineers in this task [8].

The metallic corrosion products can be generated as both large particles ($>0.003 \mu\text{m}$) or small particles and/or volatiles. Even with current state-of-the-art point-of-use filters, metallic contamination will still enter the process tool. As device geometries continue to decrease, future work will have to focus on addressing technological requirements for the removal of these small particles and volatiles. This research shows that as a system stabilises the contaminants are likely to be small particles and/or volatiles.

The tests have shown that Hastelloy performs slightly better than 316L EP-SS, however Hastelloy is a more expensive material to purchase and fabricate. Given the miles of corrosive gas piping required in a fab, running the entire system in Hastelloy would involve major additional capital expenditure. One solution would be to use Hastelloy on the parts most likely to come into contact with moisture, e.g. at cylinder manifolds.

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