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Characterisation of aqueous ferric chloride etchants used in industrial photochemical machining

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Abstract

Ferric chloride ($FeCl_3$) is the most commonly used etchant for photochemical machining (PCM) but there is a great variety in the grades of the commercial product. This paper aims at defining standards for industrial etchants (that are not chemically pure) and methods by which they are analysed and monitored.

In an ideal world, to maintain a constant rate of etching and hence control of part dimensions dependent on etch time, the etchant composition would be constant. Unfortunately, in the real world, the etchant composition changes continuously. As an *n*-valent metal (M) is dissolved into solution, etchant is consumed and the by-products of ferrous chloride ($FeCl_2$) and metal chlorides (MCl_n) are generated, i.e.

$$n\mathrm{FeCl_3} + \mathrm{M} \rightarrow n\mathrm{FeCl_2} + \mathrm{MCl}_n$$

Thus, for quality control (QC) of PCM, this creates a specific demand for data relating to the composition of the etchant as it changes. The demand covers characterisation of the virgin etchant, its degradation with use and the etchant resulting from its in situ chemical regeneration.

There are various parameters that are typically measured in commercial enterprises in order to assess the quality of the etchant. These include:

- °Baumé (or specific gravity);
- temperature;
- free acid (HCl content);
- oxidation–reduction potential (ORP);
- dissolved metal content.

Variations in any of the above can affect amongst other things, the rate of etch (with a resultant change in etched dimensions) and surface finish. The intention behind the work detailed in this paper was to establish whether some of these parameters could be used to determine the etchant quality and thereby determine its fitness for purpose at any given time. Theoretically, by monitoring variations in the parameters, it should be possible to *predict* the behaviour of the etchant. This in turn would assist in deciding whether to continue etching or replace the etchant or when to regenerate it.

Keywords: Ferric chloride; Photochemical machining

1. Etchant variables

1.1. Specific gravity or °Baumé (°Bé)

While molarity of a pure solution is usually used to express concentration, in PCM the specific gravity (SG) of a virgin or used etchant can be rapidly measured by a hydrometer. This measurement is frequently converted to a °Baumé scale reading according to the equation:

$$^{\circ}\mathrm{B\acute{e}} = \frac{145(\mathrm{SG} - 1)}{\mathrm{SG}}$$

1.2. The role of free hydrochloric acid in etchants

Undesirable hydrolysis of $FeCl_3$ will occur in water according to the equation:

$$\mathrm{FeCl_3} + 3\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_3} + 3\mathrm{HCl}$$

The equilibrium can be shifted to the left by adding HCl and thus preventing hydrolysis that results in precipitation of insoluble products and spray nozzle blockage.

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Additions of HCl are also made to commercial etchants to keep metal by-products (arising from the dissolution process) in solution. In effect, the HCl acts as a source of chlorine to form metal chlorides rather than hydroxides and thereby increases the etchant's capacity for holding dissolved metals. In some etchants it is often possible to see a layer of sludge settled out on the bottom of the etchant sump. This usually suggests insufficient free acid in the formulation. The amount added is usually 0.3–0.5% HCl (w/w) but higher values may be used depending on the substrate being etched. HCl is typically added before first use of the etchant or prior to or at regeneration. Its addition not only affects the etch rate and surface roughness of the etched substrate but is also an essential component of etchant regeneration.

2. Analysis of ferric chloride etchants

2.1. Free acid content by four off-line wet chemical analytical methods

Typically, quantifying the free acid content in ferric chloride etchants involves off-line monitoring. Usually this will involve some form of manual titration. Although automatic systems do exist they are complex and expensive. An extensive literature search was made into the various titration methods used. A general overview of these methods is shown in Table 1.

Of the methods investigated, the oxalate method (emboldened in Table 1) was the best from a viewpoint of repeatability, especially for spent etchants and convenience.

2.2. Free acid content by on-line measurements of pH and conductivity

The possibility of using on-line methods to detect free acid content was investigated as a much quicker alternative to off-line methods such as titration. Monitoring the etchant condition by using probes is relatively easy, quick and does not rely on operator skill. The equipment required is specialised, although not necessarily expensive. In addition, the etchant can be monitored continuously by incorporating a data-logging facility.

Two probing techniques were used:

- pH (ORP is recorded simultaneously with the particular probe that we were using);
- conductivity.

These were used to assess whether there were any trends when measured and plotted against percentage of HCl. This would give an indication as to whether these would be valid techniques for analysing free acid content in ferric chloride etchants.

2.2.1. pH method

Ferric chloride is a particularly acidic and aggressive etchant that typically destroys conventional pH probes in a matter of weeks. In order to be able to work with this sort of medium, a pressurised probe must be used. By internally pressurising the probe to 2 bar, the ingress of $FeCl_3$ into the glass bulb is prevented and thus the service life extended. Such probes are able to survive continual immersion in etchant for periods of up to 2 years. Using a pressurised probe it was possible to measure the extremely low (and in most cases negative) values of pH.

A series of virgin etchants was made from the dissolution of GPR $FeCl_3$ solid in water to make 35, 39, 42, 45 and 49 °Bé solutions. Each was dosed with 0, 0.25, 0.5, 1 and 2% HCl (w/w). The pH was measured daily over a 7-day period and the results averaged. Fig. 1 shows a plot of average pH versus free acid content. As can be seen, HCl additions reduce the pH until, at concentrations >1%, the pH tends to stabilise.

It appears, therefore, that it is possible to use pH as a measure of free acid content for virgin etchants up to a value

Table 1
Summary of titration methods for analysing the free acid content in ferric chloride

Complexing agent	Neutralising agent	Other	Indicator used?	Method of detecting neutralisation
Sodium thiosulphate	Sodium hydroxide		Yes	Colour change
Sodium thiosulphate	Potassium carbonate		Yes	Colour change
Sodium thiosulphate	Sodium carbonate		No	pH
Potassium oxalate	Sodium hydroxide		No	pH
Potassium oxalate Potassium fluoride	Sodium hydroxide	Methanol	Yes	Colour change
Potassium oxalate **Oxalic acid**	**Sodium hydroxide**		**No**	**pH**
Potassium fluoride	Sodium hydroxide		Yes	Colour change
Potassium fluoride	Sodium hydroxide		No	pH
Potassium fluoride	Sodium hydroxide	Methanol	No	mV swing
Ammonium sulphate	Sodium hydroxide		Yes	Colour change
Sat. lithium chloride	Sodium hydroxide	MIBK	No	pH
Potassium oxalate Oxalic acid Organic acid salt	Sodium hydroxide		No	pH

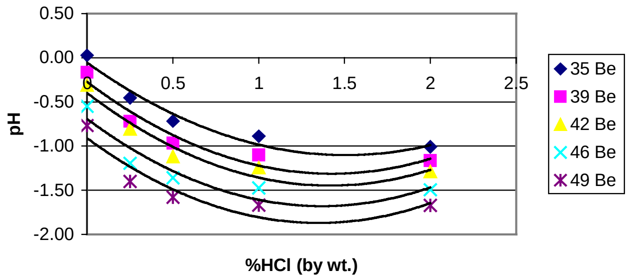


Fig. 1. Average pH vs. percentage of HCl (w/w) of virgin $FeCl_3$ solutions.

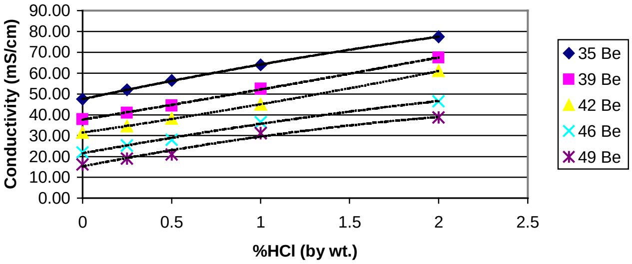


Fig. 2. Average conductivity vs. percentage of HCl (w/w) of virgin $FeCl_3$ solutions.

of 1% (w/w) HCl which happens to fall in the range for most commercial etchants.

2.2.2. *Conductivity method*

Conductance is the reciprocal of resistance and is measured in Siemens. The units of conductivity are usually measured in mS/cm for aqueous etchants.

The conductivity was monitored for various ferric chloride solutions in order to investigate the relationship between conductivity and free acid content. The conductivity electrode is not as specialised as the pH probe. The main feature is that it is made of etch-resistant material.

Fig. 2 shows a plot of conductivity versus free acid content for virgin etchants dosed with increasing proportions of HCl. As the percentage of HCl increases, the conductivity increases in a near linear manner. The slope is about 15 mS/cm per percentage of HCl.

Experimentation with Analar 45 °Bé $FeCl_3$ resulted in a similar plot (Fig. 3). Again the trend is approximately linear. All values that fall below the dotted line are attributable to the conductivity of the $FeCl_3$ alone, i.e. 0% HCl. So from this, it is possible to work out conductivity due to H^+ (from the free acid) alone as these values occur above the dotted line.

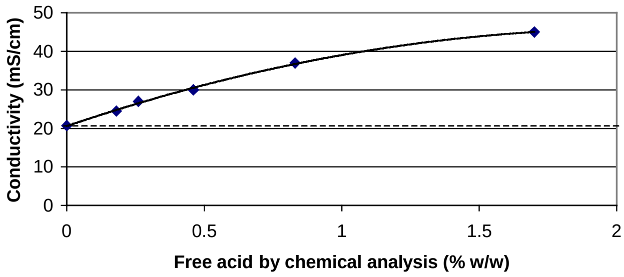
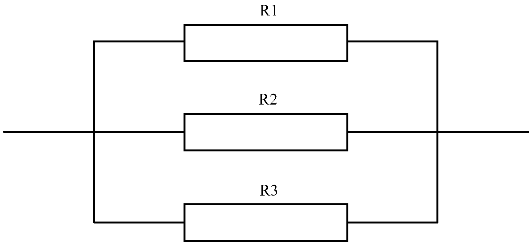


Fig. 3. Conductivity vs. free acid content for Analar grade 45 °Bé $FeCl_3$ (at 20 °C).

When viewing the system as an electric circuit, the components of the etchant can be considered as individual resistances in parallel:



where R_1 is the resistance due to $FeCl_3$ (Fe^{3+}), R_2 the resistance due to $FeCl_2$ (Fe^{2+}) and R_3 is the resistance due to HCl (H^+).

Therefore, the resistance of the etchant (R_e) can be calculated from $1/R_e = 1/R_1 + 1/R_2 + 1/R_3$ and since conductivity $(C) = 1/R$, the combined conductivity of the etchant $= C_1 + C_2 + C_3$. Therefore, as there will be no $FeCl_2$ in a virgin etchant, $C_{total} = C_1 + C_3$.

The conductivity attributable to the H^+ ion alone (C_3) can be calculated by subtracting the conductivity obtained for 45 °Bé $FeCl_3$ with 0% HCl (which happened to be 20.7 mS/cm) from the conductivity measured for each of the HCl-dosed solutions. This gives rise to the plot in Fig. 4. There is a polynomial relationship between conductivity and the free acid content, as shown on the plot.

When plotting the conductivity of the H^+ versus $[H^+]$ (as obtained from the pH value), Fig. 5 is obtained. This would seem to indicate a strong relationship between conductivity and free acid for virgin etchants.

Obviously, conductivity is very much influenced by temperature. The work mentioned here was carried out at room temperature. However, an extensive amount of experimental work upon conductivity, free acid content and temperature was carried out on 35, 39, 45 and 49 °Bé $FeCl_3$. The results obtained are summarised in Figs. 6 and 7:

- conductivity increases with increasing temperature (this is to be expected as the mobility of the ions increases with temperature);
- conductivity decreases with °Baumé (as the specific gravity increases, mobility of the ions decreases);
- conductivity increases with increasing free acid content (as already shown).

2.2.3. *Resultant relationship between pH and conductivity*

A plot of conductivity versus pH is shown in Fig. 8. It appears from these investigations that the on-line monitoring of free acid may be effected by measurement of both pH and conductivity.

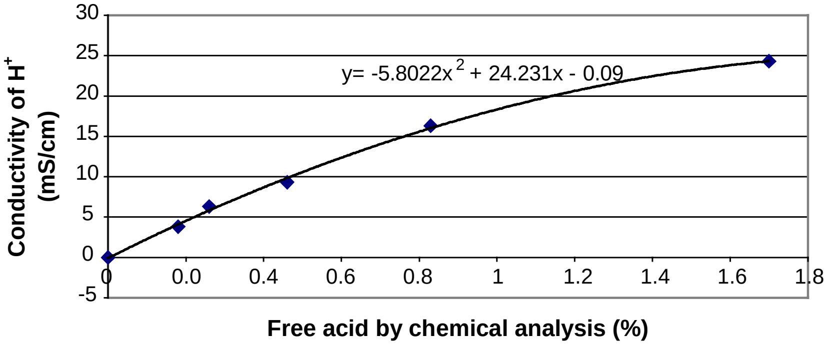


Fig. 4. Conductivity of H^+ vs. free acid content for Analar grade 45 °Bé $FeCl_3$ (at 20 °C).

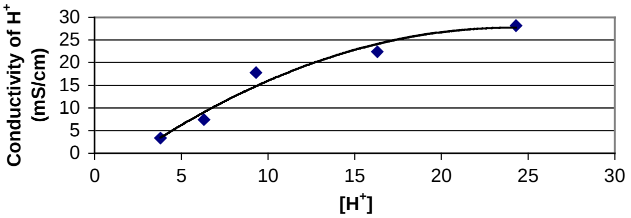


Fig. 5. Conductivity of H^+ vs. $[H^+]$ for Analar grade 45 °Bé $FeCl_3$ (at 20 °C).

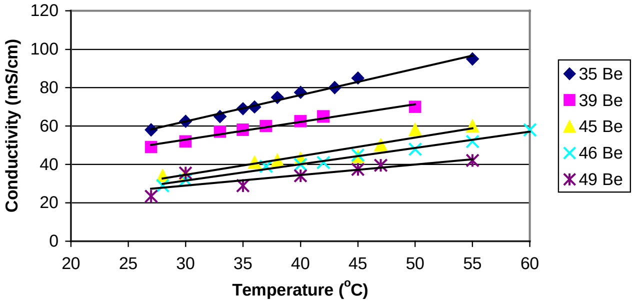


Fig. 6. Conductivity vs. temperature for $FeCl_3$ with 0% HCl (w/w).

2.3. Dissolved metal content by microspectrophotometry

Recent research has shown that dissolved metal content can be monitored economically on-line to measure dissolved nickel [1], copper [2] and stainless steel [2] in ferric chloride.

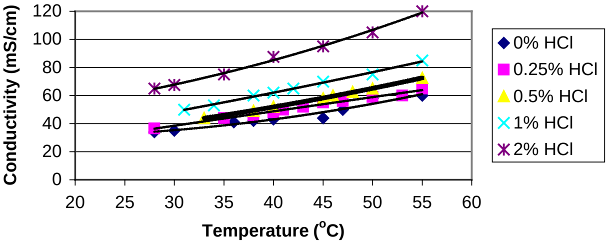


Fig. 7. Conductivity vs. temperature for 45 °Bé $FeCl_3$ for varying percentage of HCl (w/w).

2.4. Influence of temperature

Typically, temperatures of about 50 °C are used for most commercial etching applications. Etch rate increases with temperature, so it is economically viable to etch at the highest temperature that the etching machine construction materials can withstand. As most etchers are made from PVC-type materials, this limits the etching temperature to below 55 °C.

Much of the experimental work detailed in this report, was carried out at room temperature because of the difficulty of measuring small volumes of etchants in an open system at elevated temperatures without evaporation occurring. However, it was possible to carry out the conductivity measurements at higher temperatures.

For the etching of iron with $FeCl_3$, i.e.

$$Fe + 2FeCl_3 \rightarrow 3FeCl_2$$

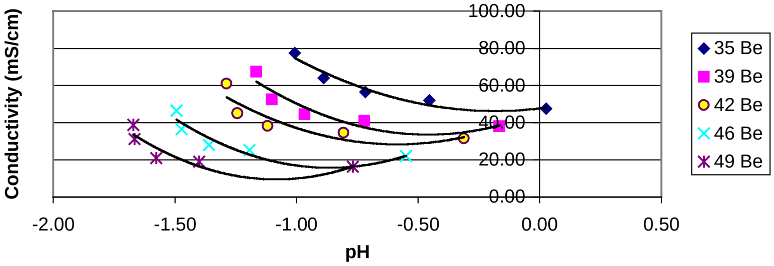


Fig. 8. Average conductivity vs. average pH of virgin $FeCl_3$ solutions.

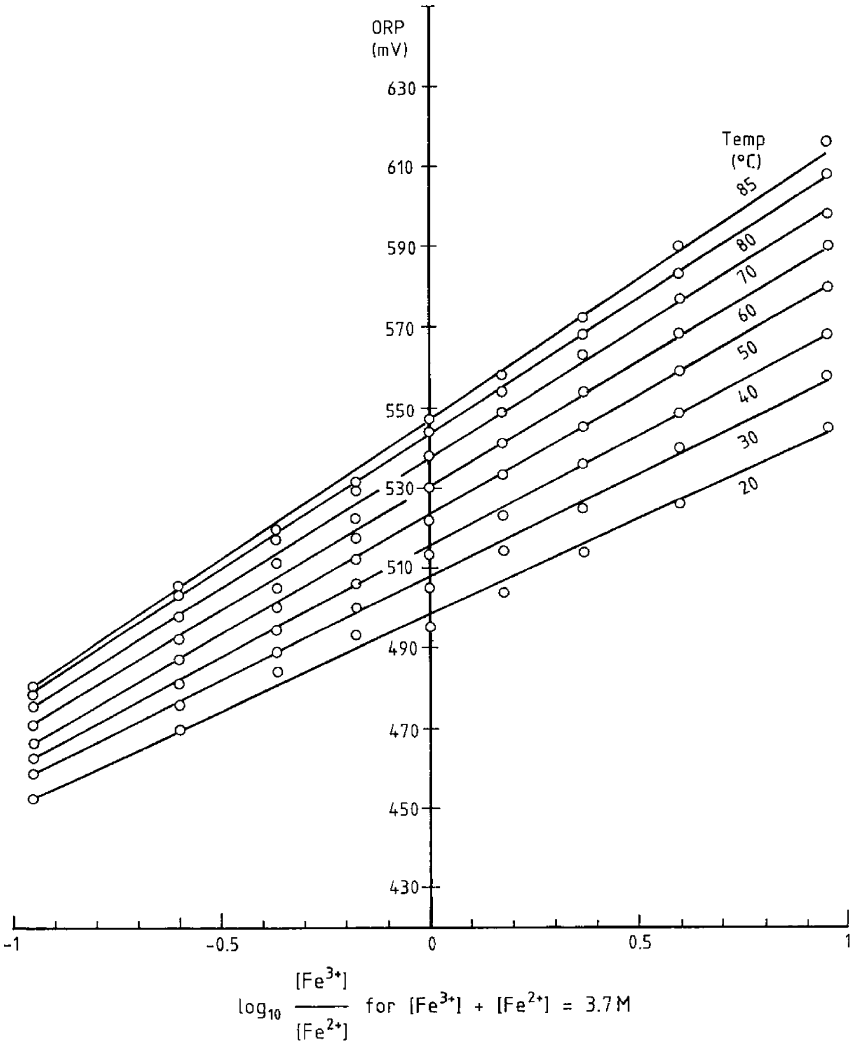


Fig. 9. ORP vs. $\log_{10}[\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}]$ for $[\mathrm{Fe}^{3+}] + [\mathrm{Fe}^{2+}] = 3.7\,\mathrm{M}$.

temperature is related to ORP by the Nernst equation:

$$E = E^0_{\mathrm{formal}} + \frac{2.303RT}{nF}\log_{10}\frac{\mathrm{Fe}^{3+}}{\mathrm{Fe}^{2+}}$$

where E = ORP (V), E^0_{formal} is the electrode potential in concentrated solutions (V), R the gas constant (8.31 J/mol K), T the absolute temperature (K), n the number of electrons changed in the redox reaction, F the Faraday constant (9.6485×10^4 C/mol), $[\mathrm{Fe}^{3+}]$ the concentration of ferric ions (M) and $[\mathrm{Fe}^{2+}]$ is the concentration of ferrous ions (M).

As can be seen from the equation, ORP increases with an increase of temperature. This is illustrated in Fig. 9, where ORP is plotted against $\log_{10}([\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}])$ [3]. Here it can be clearly seen that for any constant $[\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}]$ ratio, ORP increases with increase in temperature. The value of E^0_{formal} is given by the intercept on the y-axis of the graph, i.e. where $[\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}] = 1$.

pH is also related to temperature through the Nernst equation. A simplified form is shown below [4]:

$$E = E^0 - \frac{2.303RT}{nF}\mathrm{pH}$$

This means that the higher the temperature, the lower the pH will read. It is pointless therefore to measure pH without monitoring the temperature simultaneously.

As temperature has a direct effect on the viscosity of liquids, the mobility of ions will increase with temperature. This was indeed borne out by the experimental work, where it was shown that the conductivity of the etchant increases with temperature.

Temperature also has an effect on the etchant's ability to hold the dissolved metal content in solution. In colder climates, metal by-products can crystallise out of solution. This phenomenon has been used in the past to remove undesirable dissolved metals from solution.

2.5. Methods currently used to measure ferric chloride QC parameters

2.5.1. Ferric and ferrous ion concentration ratios by measurement of ORP

The ORP has been defined mathematically in Section 2.4 by the Nernst equation.

So for the etching of iron with $FeCl_3$, the Nernst equation becomes

$$E = E^0_{\text{formal}} + \frac{2.303RT}{nF}\log_{10}\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$$

Thus, the temperature and relative concentrations of ferric and ferrous ions will affect the ORP. For instance, from the data of Fig. 9, the model equation for 3.7 M ferric/ferrous chloride at 50 °C is

$$E = 523 + 60\log_{10}\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

Thus, if the ratio of ferric ions to ferrous ions is high (say 100, for a fresh solution) then the ORP $(E) = 523 + 60\log 100 = 523 + 120\,\text{mV} = 643\,\text{mV}$. If the ratio of ferric ions to ferrous ions is lower (say 10, for a partially used solution) then the ORP $(E) = 523+60\log 10 = 523+60\,\text{mV} = 583\,\text{mV}$. For a completely spent solution, with a ferric to ferrous ion ratio of 1, $E = 523\,\text{mV}$.

The measurement of ORP therefore gives an indication of the activity of the etchant. High values of ORP indicate an efficient etchant whilst low values of ORP indicate a slow and inefficient etchant. Ideally, we would like to maintain ORP at a high constant value for a constant etch rate of metal.

However, free acid has been found to influence ORP also, as shown in the following section.

2.5.1.1. Influence of free acid content on ORP. In order to establish the effect of free acid on ORP, a series of “virgin” etchants were made from the dissolution of general purpose reagent (GPR) $FeCl_3$ solid in water to make 35, 39, 42, 46 and 49 °Bé solutions.

Each etchant was dosed with 0, 0.25, 0.5, 1 and 2% HCl (w/w). The ORP of each was recorded on a daily basis for a period of 7 days. The average ORP was plotted against the free acid content. The ORP changed very little over a week. As can be seen clearly in Fig. 10, the addition of HCl suppresses the ORP.

Experimentation with Analar (analytical grade) $FeCl_3$, dosed with quantities of HCl up to 5% showed a similar result as can be seen in Fig. 11. A similar result (see Fig. 12) was obtained when the free acid content was verified by chemical analysis using KF and methanol [5].

As the concentration of the free acid has such a profound effect on ORP, it is therefore essential to record the two variables simultaneously in order to monitor the etchant activity accurately.

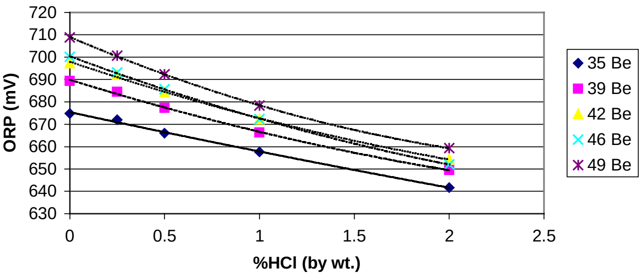


Fig. 10. Average ORP vs. percentage of HCl (w/w) of virgin $FeCl_3$ solutions.

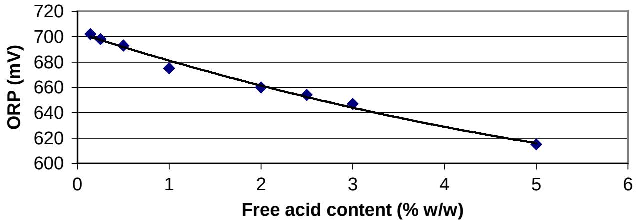


Fig. 11. ORP vs. free acid content for Analar grade 45 °Bé $FeCl_3$ (at 20 °C).

3. Conclusions: recommendations for ferric chloride QC

The obvious starting point for etchant quality control is the monitoring of incoming ferric chloride. We know that whatever parameters we need to measure, the monitoring method should be repeatable from hour to hour, day to day, month to month and even year to year. The experience gained over a 1-year research programme leads us to propose a series of rapid diagnostic tests that will confirm the etchant is within the specification desired for optimum ease of use.

We suggest therefore that the following parameters should be measured simultaneously in the as-delivered, commercial etchant prior to loading into the etching machine:

1. temperature (preferably a fixed ambient temperature);
2. °Baumé (or specific gravity);
3. ORP;
4. free acid content by

- H;
- conductivity.

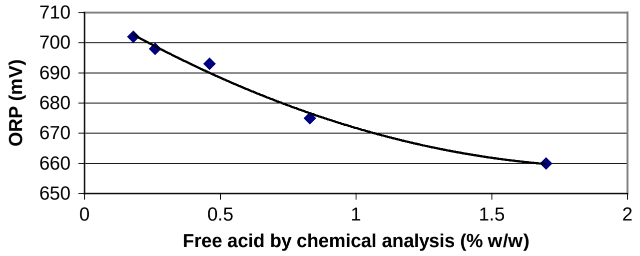


Fig. 12. ORP vs. free acid content for Analar grade 45 °Bé $FeCl_3$ (at 20 °C).

Table 2
Monitored parameters of two samples of fresh ferric chloride etchants

Fresh etchant	pH	ORP (mV)	SG (at 20 °C)	Conductivity (mS/cm)
Company A	−0.47	602	1.446	26.0
Company B	−0.47	604	1.432	28.0

Table 3
Monitored parameters of seven samples of spent ferric chloride etchants

Used etchant	pH	ORP (mV)	SG (at 20 °C)	Conductivity (mS/cm)
Company C (#2)	0.09	537	1.422	37.5
Company C (#3)	0.09	549	1.400	39.0
Company D spent	0.66	494	1.252	40.0
Company E 2	0.08	557	1.396	38.0
Company E 2 (#2)	0.12	543	1.367	47.0
Company F (#2a)	0.06	557	1.414	42.0
Company F (#2b)	0.06	590	1.402	41.0

The confirmation of the composition of the etchant can therefore be achieved at the outset of the PCM process before any etching is carried out in the new etchant. Many companies do not follow this procedure at present but we recommend it without reservation as it is cost-effective and quick. The ramifications of using an incorrectly formulated etchant in production are immense. One company spent several months trying to sort out a production problem when the cause was use of a ferric chloride solution that had been inadvertently shipped in a tanker containing remnants of a mineral acid delivery. Quick diagnostic tests would have identified the problem instantly.

From our analysis of two fresh samples of ferric chloride sent to us from the USA (see Table 2), we were somewhat surprised by their similarity.

We then discovered that both etchants had been delivered by the same supplier and thus the specifications should have been identical! This confirms the benefit of on-delivery monitoring. Any variance from anticipated values can be investigated prior to use in PCM. The slight difference in conductivities is to be expected from the slight difference in the specific gravities of the two etchants.

The values of pH, ORP and conductivity rarely occur in any supplier's data sheets. It is our recommendation that a database of measured parameters should be developed for the various deliveries and judgements on the criteria for acceptance and rejection of the etchant should be made based on the practical experience of each batch's suitability for the purpose intended.

Progressing onto the challenge of monitoring ferric chloride during the etching process, again we recommend on-line monitoring by simultaneous measurement of:

1. temperature (set by the temperature of etching);
2. °Baumé (or specific gravity);
3. ORP;
4. free acid content by pH and conductivity.

The monitoring of the etchant in the PCM process would usually be conducted at the temperature of etching. The temperature is kept high to increase the rate of etching and should be kept as constant as possible, preferably within ±0.5 °C. As etching proceeds:

- heat will be liberated from the exothermic reaction and care must be taken to cool the etchant;
- the ORP will decrease due to the consumption of ferric ions and the increase in ferrous ions;
- free acid level will fall as the HCl in solution will be driven off at the higher operating temperatures.

As etching proceeds therefore:

- °Baumé (or specific gravity) will rise as more material is dissolved in the same volume of etchant;
- ORP will fall;
- pH will rise (become more positive);
- conductivity will fall due to

1. a rise in °Baumé;
2. a fall in free acid.

It is common practice to add water into the etchant during PCM to allow for water loss by evaporation and to prevent a slowing of the etch rate. The rate of etching is usually diffusion-controlled and therefore any increase in viscosity by making the etchant more concentrated will slow down the etching of the metal. If the addition of water is maintained to keep a constant °Baumé, then conductivity will fall as free acid decreases.

Examples of etchants which appear to be spent due to a lack of free acid are shown in Table 3. The indications of a low free acid content are high values of pH (all greater than zero in the cases listed).

The complete monitoring system would then record the parameter changes as shown in Table 4.

Appropriate notes must be taken of metal types and quantities etched, and any additions of hydrochloric acid and water made that could affect the parameters being measured.

Table 4
Parameter changes over the lifetime of the etchant

Etchant state	Monitoring temperature	pH	ORP	SG/°Bé	Conductivity
As delivered	Ambient				
Fresh in machine	Etching				
Partially used	Etching				
↓	Etching				
Spent	Etching				
↓	Etching				
Optional regeneration	Etching				
↓	Etching				
Disposed etchant	Ambient				

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