

Chromium (VI) Reduction and Subsequent Sulfate Removal from Electrochemical Machining Electrolyte Systems

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Abstract - Electrochemical machining of commonly used alloys results in the production of hazardous chromium VI ions in the electrolyte. To meet health and safety standards, this chromium must be reduced to chromium III. A variety of methods and their suitability for chromium reduction are discussed here. Due to the importance of maintaining electrolyte properties for stable ECM techniques are also discussed for the selective removal of sodium sulfate, a contaminant from a common chromium reduction method.

Keywords – *Electrochemical Machining; Electrolyte Management; Chromium Reduction*

I. INTRODUCTION

Electrochemical machining (ECM) is a non-conventional machining technique which utilises anodic dissolution to remove material from a work piece, also termed the anode. An approximate negative impression of the tool, or cathode, is imprinted on the work piece during machining, meaning complex shapes and contours may be produced with one machining step. The metal is removed as ions which are dissolved in the electrolyte flushed at high speeds between the tool and the work piece. In the electrolyte these metal ions react with hydroxide ions, which is generated at the cathode surface, to form metal hydroxides which precipitate from the solution (1).

ECM is not dependent on the mechanical characteristics of the target material, for example, hardness. Common materials machined by ECM in industry are materials that are difficult to machine by conventional techniques; these included stainless steels and super-alloys, e.g. Inconel 718. (2) These alloys contain chromium to prevent the alloy from corroding in their working environment. (3) Chromium's most stable valence in aqueous solutions is chromium (VI) and is highly soluble. (4) This ion is toxic and a known carcinogen when inhaled, ingested or skin contact is made. (5) As such, ECM working areas are contained to prevent electrolyte splashing and gases produced can be safely exhausted away from the machining environment. However, to prevent the ECM operators from being exposed to high levels through contact with the parts, the chromium (VI) concentration is maintained at low levels by reducing it to chromium (III). Cr(III) is less toxic and less soluble than its toxic counterpart, allowing the chromium to be removed via

filtration along with the other metal hydroxides generated by ECM. (5–8)

Small gaps between the anode and cathode are maintained during the ECM process. (9,10) The electrolyte is flushed through to remove machining products which may clog the gap causing short circuits. (1) Short circuits will damage both the tool and the work piece. It is for this reason that the electrolyte is filtered of solid particulates.

There are a range of methods available for chromium reduction/removal, from solvent extraction, ultrafiltration, electrodialysis, ion exchange, photocatalytic reduction and chemical precipitation (11); these will be discussed in more detail in this article.

ECM is a sensitive process; small changes in electrolyte conditions can greatly affect the machining results. The temperature, pH, conductivity and composition of the electrolyte should be maintained within acceptable limits dependent on the required accuracy and precision of the final product.

Maintaining the temperature, pH and conductivity of the electrolyte are all relatively easy, however, maintaining the electrolyte composition can be difficult due to the chromium reduction technique. Most of the available or suitable techniques add unwanted ions to the electrolyte. A common contaminant from chromium reduction is the sulfate ion (12). Sulfate is highly soluble (13) and can affect the machining characteristics of some metals and alloys due to the differing behaviour of the sulfate ion to the predominant anion in the electrolyte. Sulfate concentrations can build up to beyond that of the intended electrolyte base e.g. sulfate levels can exceed nitrate levels in a sodium nitrate electrolyte due to chromium reduction with a sulfur containing chemical.

To minimise waste and costs of replacing electrolyte when the sulfate concentrations surpass acceptable levels, sulfate can be removed from the electrolyte. There are a number of ways to remove sulfate ions from the electrolyte; established methods and a new method will be discussed in this paper.

A. Chromium (VI) Reduction Methods

Concentrations of chromium (VI) in waste water are highly restricted by law due to its toxicity and environmental impact, as such, many methods have been developed to reduce and remove chromium.

Zhang et al. have demonstrated that Cr(VI) can be removed from an aqueous acidic electrolyte via solvent extraction with tri-n-butyl phosphate (TBP) in kerosene (14). They showed that one Cr(VI) could be complexed by 3 TBP molecules. The presence of sodium chloride in the aqueous phase improves the extraction efficiency. This technique may not be suitable for managing the electrolyte system of an ECM process as small amounts of the non-aqueous phase may mix with the aqueous electrolyte contaminating the electrolyte. This method would be best suited to small electrolyte quantities, not the large scale quantities needed in industry. This also does not address the reduction of Cr(VI) to Cr(III) so a follow-up step must be added to address this.

Membrane separation, or ultrafiltration, of Cr(VI) has been demonstrated by a number of authors (15–17). Here they utilise positively charged membranes to adsorb Cr(VI) on the surface of the membrane as the electrolyte is passed through the membranes. Once the membranes are saturated, the Cr(VI) can be removed from the membranes as a concentrated solution and subsequently treated to reduce the Cr(VI). This is more suited to an application where waste water is treated to be released to reduce the volume of hazardous waste to be disposed of. Large amounts of Cr(VI) are generated in an industrial sized ECM facility due to the alloys generally machined having high percentages of chromium (> 11 %); if membrane separation were to be employed in such a position, the number of filters would be impractical or the membranes would foul easily and require frequent cleaning or replacement. Membrane filtration is ideal for low concentrations of Cr(VI).

Ion exchange membranes have also been shown to be suitable for Cr(VI) removal. (8,11,18) Ion exchange membranes, as their name suggests, exchange an ion from the membrane into the solution which is replaced by the Cr(VI). This may or may not be a suitable choice for managing ECM electrolytes depending on the electrolyte choice. Usually, the anion exchange resin to capture Cr(VI) uses chloride as the exchange ion(18). Chloride based electrolytes are known as active electrolytes and behave differently to passive electrolytes(9). Extended use of ion exchange membranes from chromium treatment will change the characteristics of the electrolyte. Ion exchange membranes have also only been demonstrated to remove trace and milligram amounts of Cr(VI) from solution but they are highly selective in the ions they target. (11)

Electrodialysis was utilised by Peng et al.(19) to remove trace amounts of Cr(VI) from electrolyte. Electrodialysis is a membrane separation technique which uses electrical driving forces for the migration of ions through ion selective membranes. This creates a concentrated stream in which Cr(VI) can take place. Again this technique is only suitable for low concentrations as the membranes foul quickly.

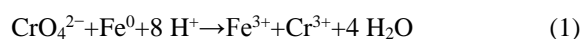
Photocatalytic reduction is also used to reduce Cr(VI) to Cr(III)(20). Purifics Complete Water Purification have developed a system which uses titanium dioxide and UV light to reduce Cr(VI). The system is fully automated and

can reduce chromium concentration to 1 ppb. The system does not create any liquid waste streams. Cr(III) is adsorbed on the TiO₂ catalyst which is processed afterwards to recover the TiO₂ for reuse and a highly concentrated Cr(OH)₃ sludge. This is an ideal solution for chromium reduction but one of the disadvantages is the high capital cost. The unit is also quite large, taking up a considerable amount of floor space.

Biological hexavalent chromium reduction is another available method (21,22). This involves using bacteria as the reducer. This is often done as a batch process but can also be used in a continuous flow system. This is often used to treat industrial waste before it is fed back into the national water system. It would not be suitable to introduce bacteria to a system where the water is used for long periods of time as it is in ECM where their presence could be spread to other machines or hinder machining due to the bacteria size which in some cases may be comparable to the inter-electrode gap maintained during machining.

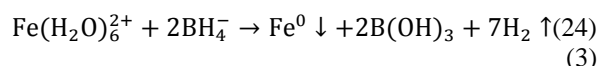
The most common method to reduce hexavalent chromium is chemical reduction and precipitation. (12) Trivalent chromium is stable at low pH so most reductions take place at low pH and then the pH is raised to precipitate trivalent chromium hydroxide. There are several options within this category some of which will be discussed in more detail here.

Elemental iron can be used to reduce Cr(VI)(23,24); to increase the contact area iron powder is the most suitable form to use. The reaction proceeds by the following mechanism:



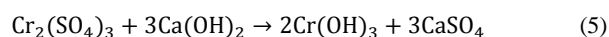
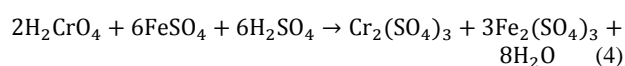
This method creates lots of sludge waste and requires an excess of elemental iron to reduce chromium concentrations to acceptable levels.

Ferrous sulfate heptahydrate (FeSO₄·7H₂O) and sodium borohydride (NaBH₄) are added together; sodium borohydride reduces the ferrous sulfate to nanoparticles of zero-valent iron(25,26).



The elemental iron particles produced then reduce the Cr(VI) in the same way as in the previous method. As such, this method also produces large amounts of solid waste which can be costly to dispose of correctly.

Another iron based method for reducing Cr(VI) is using ferrous sulfate in an acid environment followed by precipitation. It proceeds by the following reaction (5,27):



Precipitation of $\text{Cr}(\text{OH})_3$ can be caused by adding $\text{Ca}(\text{OH})_2$ as shown in the mechanism or with NaOH . The advantage of using calcium hydroxide is the precipitation of the sulfate as calcium sulfate alongside the chromium (III) hydroxide which slows the build-up of sulfate in the electrolyte over time. However, even small amounts of calcium in the electrolyte can cause issues with electrolyte flow. Electrolyte in ECM is forced through very small gaps at high speeds; under these conditions calcium compounds may precipitate(28) causing restrictions of the electrolyte flow and cause sparks in the working gap (29). It could also cause premature fouling of the filters removing particulates from the electrolyte. Whilst this may be an appropriate method in other industrial environments, it should be avoided for ECM conditions.

Calcium polysulfide (CaS_5) is also capable of reducing $\text{Cr}(\text{VI})$ but suffers from the same issues mentioned with $\text{Ca}(\text{OH})_2$ (6). This reduction takes place at pH between 8 and 10 which may be preferable in some cases

There are a number of other sulfur containing compounds that can reduce $\text{Cr}(\text{VI})$; Kaprara et al (12) discusses these in detail. The authors reported the highest reduction efficiency for sodium sulfide and sodium dithionite in the pH range of 6-8. Using Na_2S has been reported to release an unpleasant odour; this is not advisable in a machining environment where many people may be exposed to the odours. Using sodium dithionite as the reductant will result in the accumulation of sulfate in the electrolyte, gradually altering the properties of the electrolyte.

B. Sulfate Removal Methods

As with chromium reduction, there are a number of known methods to remove sulfate ions from an aqueous medium.

In the water treatment industry the range of treatments vary, though the main basis for the available methods will either be precipitation or membrane removal.

Among the membrane removal techniques are reverse osmosis, electrodialysis and nano-filtration (30). For reverse osmosis to be effective, the concentration of calcium and sulfate must be low in order to prevent scaling of the membrane (13). Reverse osmosis is usually used in the production of ultra-pure water as it unbiasedly removes all ions from water. This is not suitable for managing ECM electrolyte systems where selective removal of sulfate, in this instance, is required.

Electrodialysis can also be used to purify water(13). As said in the previous section, electrodialysis utilises an electrical potential to drive the migration of ions through selective membranes. These membranes can be selective, though the membranes will need frequent replacement due to the amount of sulfate generated in a full scale ECM production line machining alloys with high chromium content and the subsequent reduction of chromium.

Nano-filtration units are commonly installed on oil and gas stations where high salinity but low sulfate water is required (31). The water needs to be free from sulfate to prevent barium and strontium scale in the oil/gas well. Typical seawater contains only 2.65 mg/L(32); sulfate concentrations in ECM electrolyte can be thousands of times higher than this. Nano-filtration uses membranes with pores slightly larger than those used for reverse osmosis, so they allow a higher number of ions to pass through. Separation occurs due to size exclusion and electrostatic interactions for charged species (31). Whilst this technique may be suitable to treat sea water for use in oil and gas wells, the concentrations of sulfate in ECM waters are just too high to make this method a realistic option.

There are also a few options for precipitation of sulfate. Sulfate can be precipitated as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) through a means of ion exchange removal and saturation by mixing the pure cation/anion streams(13). However, this process is only suitable up to 2000 ppm(13) which is far below the concentrations seen in ECM electrolytes.

Sulfate can be removed from solution through the precipitation of insoluble sulfate salts; commonly these salts are gypsum(13,33), barite (BaSO_4 (13)), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$)(13,34). To precipitate sulfate as gypsum, calcium nitrate is added. Calcium has a higher affinity for sulfate but is sparingly soluble and drops from the solution. Barium chloride is added to precipitate barite; calcium hydroxide ($\text{Ca}(\text{OH})_2$) and aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) are added to precipitate ettringite. As previously mentioned, adding calcium and barium to an ECM system should be avoided as it can cause blockages in the electrolyte flow due to precipitation in high flow, low pressure areas.

Sulfate can also be precipitated as sulfur or sulfide through a biologically mediated reduction (13,35). There are a series of sulfate reducing bacteria which may be added to the electrolyte to keep the sulfate concentrations under control. These bacteria release hydrogen sulfide gas (35) which not only has a pungent smell but it is toxic and flammable. This should be avoided in a machining environment so this method is not suitable for ECM electrolyte management systems.

This paper will discuss a number of alternative methods to remove sulfate which have been investigated experimentally with varying levels of success.

II. METHODOLOGY

A. Low Pressure Precipitation:

An electrolyte consisting of 5 % wt NaNO_3 and 5 % wt Na_2SO_4 is made up with 18.2 MΩ cm purified water. Around 100 mL of solution was placed in a 500 mL beaker which was placed into a vacuum desiccator. The sample was left in the vacuum desiccator with the vacuum pump attached for a minimum of 30 minutes.

B. Precipitation with Calcium Nitrate

An series of electrolytes were made consisting of a range of NaNO_3 (2.7 -13.7 %) and Na_2SO_4 (0.17 -5.9 %) concentrations and 18.2 M Ω cm purified water. A small amount of sodium carbonate was also added as this is a small contaminant of one of the reagents used for the chromium reduction. A portion of the electrolyte was removed and reduced in volume by a specified concentration factor via evaporation before being allowed to cool to room temperature again. Either a fast or slow heating regime was implemented for the volume reduction. A corresponding amount of calcium nitrate was added whilst being stirred for 5 minutes before the precipitate was removed via filtration. Samples of the electrolyte were collected throughout for chemical testing by Chemtest Ltd to determine how nitrate, sulfate, carbonate and calcium concentrations varied. See Table 1 for the quantities of each salt, the concentration factor used and the heating regimen employed for each run.

All chemicals were ACS grade reagents from Sigma Aldrich and the purified water was from an ELGA PURELAB Option-Q water purifier.

III. RESULTS AND DISCUSSION

Maintaining the properties of the electrolyte is crucial for stable electrochemical machining; one of the most efficient chromium reduction methods results in the accumulation of sulfate over time. If, for example, the electrolyte begins as sodium nitrate, a passive electrolyte, the nature of the electrolyte will gradually transform to an active electrolyte as sulfate builds up. If the sulfate cannot be removed effectively, without removing or adding other ions to the solution, the only option is to replace the electrolyte. This is an expensive solution as the electrolyte must be disposed of according to the appropriate laws, plus the expense of the new chemicals and ultrapure water.

The methods discussed above are either impractical for the concentrations of sulfate generated in an industrial scale ECM establishment or removes other important ions, e.g. nitrate, which would need to be replaced.

A. Low Pressure Precipitation

It is known that carbonate and sulfate salts precipitate in low pressure, high shear areas in a flowing liquid; it was prepositioned that this phenomenon could be utilised to selectively extract these salts from a nitrate based electrolyte used for electrochemical machining to minimise the frequency of electrolyte changes required in an ECM set up.

In this experiment 100 ml of a 5 % wt. NaNO_3 + 5 % wt. Na_2SO_4 solution vacuum desiccator for 30 minutes. There was no evidence of precipitation after this time; however, this is most likely because the solution was stagnant and not flowing at high rates. A limit was placed on the length of time the sample was under vacuum as any solution to remove excess sulfate which may be employed in industry should be quick and easy so as not to disrupt the ECM process.

B. Precipitation with Calcium Nitrate

Calcium nitrate can be added to a solution to remove sulfate and carbonates as a precipitate. Calcium nitrate is highly soluble; however, calcium has a higher affinity for these carbonate and sulfate over nitrate; these salts have limited solubility. As such, calcium carbonate and calcium sulfate should precipitate from the solution.

The effects of total nitrate concentration, total sulfate concentration, the concentration factor employed, the rate of volume reduction and the temperature of the solution when the calcium nitrate is added on the efficiency of sulfate removal.

The nitrate, sulfate, carbonate and calcium concentration is measured before and after the calcium nitrate addition by sending water samples to Chemtest Ltd for testing. These results can be seen in

The notation in

for example, is as follows; sample 1-2 indicates that the sample is from experiment run 1 before the calcium nitrate has been added; sample 1-3 indicated the sample is from experiment run 1 after the calcium nitrate has been added. The difference column shows the concentration difference before and after the calcium nitrate addition apart from the carbonate concentration. In all instances, the carbonate concentration is below the detectable limit indicating that all of the carbonate had been removed by the addition of calcium nitrate regardless of the experimental run. Experiment 5 is a little different in that the calcium nitrate was added before the reduction step but whilst the electrolyte was at 60 °C which means that the calcium nitrate had already been added when the sample 5-2 was taken.

In the majority of cases the concentration of nitrate increases which is to be expected due to the additional nitrate added through the calcium nitrate. However, where the solution was reduced in volume by 2 or 4 times, the nitrate concentration decreased after the calcium nitrate was added. It is possible the saturation limit was reached in test 3 where the volume was reduced to just one quarter. This could have caused co-precipitation of other salts, including sodium nitrate, below their saturation limits. The time taken for the liquid to cool to room temperature may also have had adverse effects on the concentrations. However, further examination is needed to understand this result fully.

The calcium concentration across the full 8 experiments increases or there is no change between the two samples. This is to be expected because there should be little to no calcium present in the electrolyte before the addition of calcium nitrate. With experiment 5 this is not true as calcium nitrate was added before the volume reduction step and hence before the sample was taken for analysis. This explains why there is no change in the calcium concentration for experiment 5. It is unfavourable having even a small concentration of calcium in the electrolyte due to its low solubility with carbonate and may cause precipitation problems in small electrolyte inlets.

The main interest of this study is the change in sulfate concentration by the addition of calcium nitrate. As can be seen by, there is no real pattern. In some instances the sulfate concentration increases after the calcium nitrate addition, in others it decreases. In all instances, however, the change is minimal, decreasing by a maximum of 5000 mg/l and increasing by a maximum of 400 mg/l. The largest decrease occurs where the highest initial sulfate concentration was used. This is likely because the solubility limit of calcium sulfate has been reached which causes any excess beyond this limit to precipitate, which is exhibited as a decrease in the sulfate concentration.

From these experiments, it can be said that the addition of calcium nitrate is not an efficient technique for the removal of sulfate from electrolyte regardless of how the electrolyte is pre-treated as very little sulfate is removed. It's also highly likely that calcium would accumulate in the electrolyte with multiple treatments which would cause problems with precipitation and clogging of small pores in cathodes or electrolyte cleaning membranes.

IV. CONCLUSION

Electrochemical machining of super alloys invariably produces toxic hexavalent chromium. There are environmental laws regarding the concentration of hexavalent chromium permitted in industrial waste waters. Due to this, there has been much research into various techniques to reduce Cr(VI) to the less toxic Cr(III) form. In an electrochemical machining situation where employees are exposed to the electrolyte through contact with machined parts it is important to keep the concentration of Cr (VI) low in addition to meeting the release laws.

Chemical reduction and precipitation is the most viable option to treat the electrolyte in an ECM industrial environment due to the volumes and concentrations encountered. Research by Kaprara et al. showed that sodium dithionite provided the most efficient reduction of Cr(VI) from a range of sulfur containing compounds. This reduction causes the accumulation of sulfate in the electrolyte which, over time, changes the characteristics of the electrolyte which in turn affects the machining quality.

Electrolyte in ECM is reused for long periods of time. This is only possible due to complex electrolyte management systems which clean and maintain the electrolyte properties. To ensure longer shelf life of the electrolyte, it is important to selectively remove the sulfate too.

This paper discussed two options for sulfate removal; one using low pressure and the other using precipitation with calcium nitrate. Both methods were unsuccessful.

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Table 1: Experimental parameters for calcium nitrate precipitation tests

Experiment number	Mass of sodium nitrate (g)	Mass of sodium sulfate (g)	Mass of sodium carbonate (g)	Concentration factor	Mass of calcium nitrate (g)	Speed of heating
1	82.253	1.774	0.166	3	0.784	Fast
2	82.253	59.146	5.511	3	20.969	Fast
3	82.253	1.774	0.166	4	1.165	Fast
4	82.253	1.774	0.166	2	0.403	Fast
5*	82.253	1.774	0.166	3	0.784	Fast
6	137.088	1.774	0.166	3	0.784	Fast
7	27.418	1.774	0.166	3	0.784	Fast
8	82.253	1.774	0.166	3	0.784	Slow

* the solution was maintained at 60 °C whilst the calcium nitrate was added before the temperature was raised to allow the solution to reduce in volume under rapid boiling. The solution was cooled before filtration.

Table 2 chemical analysis conducted by Chemtest Ltd for nitrate, sulfate, carbonate and calcium concentration

Deter minand	U nits	limit of detection	1-2	1-3	diff erence	2	2	diff erence	3	3	diff erence	4	4	diff erence
			-2	-3		-2	-3		-2	-3		-2	-3	
Alkalinity (Carbonate)	mg CaCO ₃ /l	10	20	< 10		1	<		3	<		2	<	
			5000	10					7	10		1	10	
Nitrate	mg/l	0.50	87000	120000	-33000.00	1	1	-	1	1	200	8	7	120
						50000	90000	40000.00	60000	40000	00.00	4000	2000	00.00
Sulphate	mg/l	1.0	430	4500	-	2	2	500	5	5	-	2	2	-
Calcium	mg/l	5.0	11	3400	-	4	1	-	1	4	-	1	1	-
					3389.00	6	800	1754.00	8	600	4582.00	6	500	1484.00
			5-2	5-3	ifference	6-2	6-3	difference	7-2	7-3	difference	8-2	8-3	difference
Determinand	U nits	limit of detection												
Alkalinity (Carbonate)	mg CaCO ₃ /l	10	< 10	< 10		<	<		1	<		2	<	
						10	10		10	10		0	10	
Nitrate	mg/l	0.50	110000	120000	-	1	1	-	4	5	-	1	1	-
					10000.00	50000	70000	20000.00	1000	2000	11000.00	00000	20000	20000.00
Sulphate	mg/l	1.0	4200	4600	-	4	4	400.	4	4	-	4	4	200.
					400.00	800	400	00	400	800	400.00	400	200	00
Calcium	mg/l	5.0	2100	2100	0.00	1	2	-	5.	2	-	9.	2	-
						7	700	2683.00	4	400	2394.60	8	400	2390.20