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Production and Analysis of Recycled Ammonium Perrhenate from CMSX-4 superalloys

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Abstract: The process to extract rhenium from a superalloy is an immense technical challenge due the complex chemistry involved. Being one of the rarest elements in the earth's crust the scarcity and cost of rhenium makes it advantageous to recover the element from scrap superalloy. In this research the separation and monitoring of the different stages of the recycling process to extract rhenium from CMSX-4 superalloys using a distillation process were performed. This novel method combining distillation and use of exchange resins was used to separate rhenium from a complex mixture of metals in the CMSX-4 superalloy. The identification and quantitation of perrhenate and contaminants were performed by atomic absorption spectroscopy (AAS), Fourier transform infrared spectroscopy (FTIR), ion chromatography (IC) and Scanning Electron Microscopy- Energy Dispersive X-Ray (SEM-EDX). Perrhenate ions were extracted with purity close to 93%. The analytical characteristics for a novel infrared method to quickly identify perrhenate anions from CMSX-4 are presented. The main characteristics of the analytical validation were: LoD: 0.5% w/w; LoQ: 1.5% w/w; linear range 1.5-100% w/w; correlation coefficient $R^2 = 0.9905$; precision (%RSD) for 10%w/w = 6.6 and 75%w/w = 4.1, respectively; accuracy (%) for 10% w/w 99.6% and 75% w/w=101.1, respectively.

Keywords: Rhenium; CMSX-4; superalloys; metal recycling; metal separation.

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1 Introduction

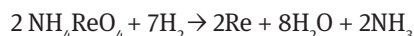
A super alloy, being a unique high temperature and high performance alloy, displays excellent resistance to mechanical and chemical degradation close to their melting points [1]. In addition, super alloys demonstrate increased mechanical strength, creep resistance at high temperatures, good surface stability, and corrosion and oxidation resistance. Furthermore, as they maintain their properties at elevated temperatures (above 540°C), super alloys can be employed in the hottest sections of turbines [2]. As a consequence of technological advances in super alloys, manufacturing costs have increased. Moreover, super alloys require the use of rare and expensive elements, such as rhenium or ruthenium. The alloying elements and heat-treatments also often make superalloys difficult to machine and weld, increasing fabrication costs, part reject rates, and reworks [3].

Rhenium is one of the rarest and most valuable elements in nature, and can only be found distributed on the earth's surface in very small quantities, on the order of 10⁻⁹% [4]. Moreover, it occurs in a scattered form, and methods for its separation – in the form of metal or compounds – are complicated and costly. These factors result in a high price for rhenium and its compounds. Rhenium can be found in copper sulphide ores, but predominantly it can be obtained through molybdenum refinement. After its isolation, rhenium is traded commercially as sodium and ammonium perrhenates. In addition to its use in super alloys, specific properties of rhenium also make it useful for other selective applications, including catalysis and radiology and applications in the nuclear industry.

Rhenium has a range of very desirable mechanical properties that makes it a valuable alloying element. This element has an extremely high density of 21.04 g/cm³, a melting point of 3180°C and a boiling point of 5630°C [5]. Another useful mechanical property is its high ductility, and it does not exhibit a ductile/brittle transition, so it remains ductile up to its melting point. It also presents high strength at elevated temperatures together with a high modulus of elasticity. Rhenium has excellent creep

resistance due to its high re-crystallisation temperature of 2800°C, and it withstands vigorous thermal cycling without deterioration.

Being so rare and costly to extract makes it advantageous to recover rhenium from scrap superalloy material. This scrap can take the form of worn component parts or the waste material resulting from the casting process in the production of component parts [3]. The process to extract rhenium from a superalloy is a technical challenge due to its complex chemistry, such as the high melting point of the superalloy itself and the high number of oxidation states of other metals present in the mixture. Rhenium, with electron configuration $[\text{Xe}] 4f^{14} 5d^5 6s^2$, has nine known oxidation states ranging from -1 to $+7$. The most common rhenium compounds are the oxides and the halides, exhibiting a broad oxidation number spectrum. Once extracted, rhenium is commercially traded in the form of ammonium perrhenate (APR), a white, water soluble salt (NH_4ReO_4). Rhenium can be obtained from ammonium perrhenate by reducing the salt with hydrogen at high temperatures following the reaction:



Some studies have been proposed to examine the extraction of rhenium from different matrices. Three major themes emerge repeatedly throughout the literature for the hydrometallurgical extraction of rhenium - solvent extraction, ion exchange and distillation. Zhan-Fang et al. [6] recovered rhenium from an alkaline leach solution of an ore containing rhenium and molybdenum by repeated solvent extraction to obtain rhenium salts with an efficiency of 96.8% [6]. The feed solution in this work came from leaching an ore sample with a composition of molybdenum, 47.4%, and rhenium, 0.07%, the remainder being S, Cu, P, Fe, As, CaO, SiO_2 and Sn.

Other methods found in the literature include the extraction of perrhenates using an ion exchange column. Studies outlined by Leszczynska-Sejda et al. [7] suggested two methods for the synthesis of perrhenic acid and its extraction: the sorption of the perrhenate ion on selective anion exchange resins and the sorption of ammonium ion on selective cation exchange resins. The latter was more effective, producing yields of 88%, whilst the former proved ineffective, producing yields that never exceeding 6%. Low levels of contaminants, including NH_4^+ , Na^+ , K^+ , Mg^{+2} and Ca^{+2} , were found in the extract.

Koyama [8] studied the separation of rhenium from technetium by a distillation method due to the similarity in chemical properties of the two elements. Steam distillation was found to be the most effective method

for this particular experiment. The samples used in this procedure were pure standards; the purity of the product was not stated within the paper, although they stated that almost 100% of the rhenium was distilled out.

The analysis of rhenium and rhenium salts traditionally has been performed using atomic techniques, such as Atomic Absorption Spectroscopy [9,10]. More recent methods have used inductively coupled plasma mass spectrometry (ICP-MS) to determine rhenium in water [11] and geological materials [12]. Extended X-ray Absorption Fine Structure (EXAFS) has also been used to study the structural properties of rhenium complexes and to interpret extraction mechanisms [13]. Electrochemical analysis of rhenium has also been developed in order to estimate rhenium content in the liqueur from the process of recycling catalysts [4].

The use of spectroscopic techniques for the analysis of the different rhenium complexes using Raman has been also studied [14]. However, these studies are not so abundant for perrhenates (Re (+7)). The most recent study in this sense is attributed to Gassman et al. [15], who presents the capabilities of rhenium as a surrogate material for the safe disposal of technetium in the nuclear industry. Even less information can be found concerning the infrared analysis of perrhenates [14]. Palant et al. [16] developed some work on the infrared analysis of organic complexes using Re (+7) in order to favour its extraction from acidic solutions. Further work has been developed in this area by Cao et al. [17] who used complexes to selectively trap perrhenate and pertechnetate before IR analysis.

The importance of recycling and recovery of metals from used materials is growing. Mining costs and the difficulty of access to some ores makes recycling a more economically viable alternative for many metals. According to Hunt et al. [18], at the present rate of extraction, the reserves of rhenium will be depleted in 50-100 years. This implies that a policy of elemental sustainability and critical element recovery needs to be implemented if we want to maintain the current applications and, most important, to guarantee use for future generations. Rhenium recycling remains a challenging problem, and no definite answer has been found from an industrial point of view. To date, the most effective recycling method for rhenium in a real case is when this element is combined with platinum and recovered from automobile catalytic converters. In this case, the chemical nature of platinum and the fact this is a binary mixture makes it easy to extract, leaving rhenium behind.

In this work, the extraction and purification of rhenium from a complex nickel-based superalloy known

as CMSX-4 was investigated. For this procedure, we utilised a fractional distillation process combined with ion exchange and precipitation to produce high purity ammonium perrhenate (APR). A novel infrared method was also implemented for the fast determination of the ammonium perrhenate content in the recycled powder.

2 Material and Methods

2.1 Chemicals and methods

2.1.1 Dissolution and distillation method

CMSX-4 is a second generation nickel-based superalloy with a typical composition of: chromium (6.5%), cobalt (9.6%), tungsten (6.4%), rhenium (3%), molybdenum (0.6%), aluminium (5.6%), titanium (1%), tantalum (6.5%), hafnium (0.1%) and nickel (60.7%). In order to extract the different metals from the superalloy aqua regia, a mixture of concentrated hydrochloric acid (36%, 11.65 M) and concentrated nitric acid (70%, 15.8 M) in a 3:1 ratio, was used. Both acids were purchased from Merck (Darmstadt, Germany). One hundred grams of CMSX-4 were mixed with one litre of the aqua regia solution in a polypropylene container and placed in the fume cupboard using a venturi scrubber to prevent any release of gases to the environment for 5 hours. Any solids produced at this stage were removed and the supernatant transferred to another container. The next stage consisted of the sequential addition of NaOH (Merck) pellets to the metal solution. This was performed under constant stirring and pH monitoring until the solution reached pH 13. The various solids obtained during the sequential precipitation after sodium hydroxide addition were removed. The supernatant was then subjected to both a clean-up and pre-concentration process using a Dowex Marathon A: Type 1 Strong Base Anion Exchange Resin (Dow Chemical Co) to trap the anions present in the solution. Four hundred and eighty millilitres of this solution were added to 6 grams of resin, and the mixture was stirred on a magnetic stirrer for 30 minutes. The resin was filtered from the solution and placed into a one-litre beaker with 250 mL of 21.6% HCl, and the slurry was stirred for 45 minutes. This procedure ensured the extraction of the anions absorbed on the resin into the solution. The final step prior to distillation was filtering off the resin to leave a solution containing the target analyte, perrhenic acid, and other residual anions.

Three hundred and fifty millilitres (350 mL) of the enriched perrhenic acid solution were placed into a

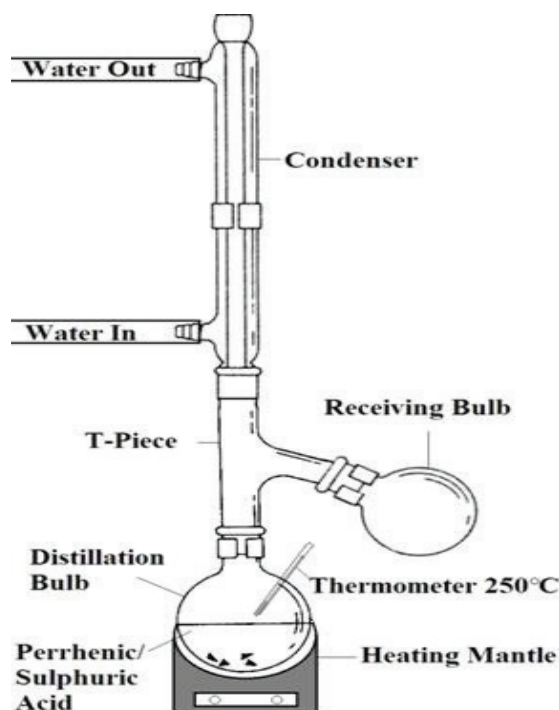
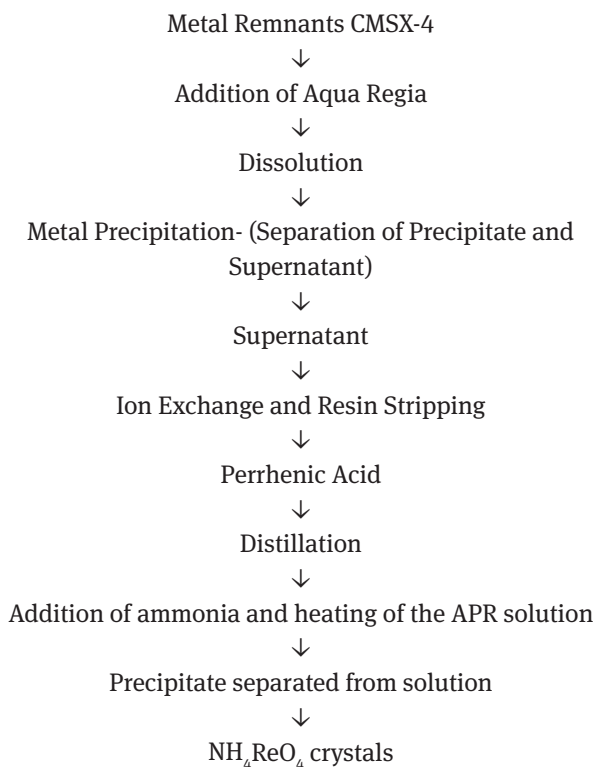


Figure 1: Distillation set up for the separation of perrhenic acid in solution.

distillation bulb with 50 mL of concentrated sulphuric acid using a distillation setup as shown in figure 1. The temperature was recorded until the system reached 185°C, when the source heating was turned off and the system allowed to fully cool down. The collecting bulb containing this first fraction was then removed and replaced with a new bulb. An additional 350 mL of deionised water were added to the original main distillation bulb, and the mixture was carefully stirred. Heating was reinitiated and temperature recorded to repeat five cycles in total. At this point the distillation was complete. This process of sequential re-distillations serves the purpose of cleaning up the sample and obtaining a high purity perrhenic acid solution.

In order to obtain the final product, ammonium perrhenate (APR), 40 mL of concentrated (25%) ammonia solution (Merck) was added to the perrhenic acid solution obtained from the distillation process. The mixture was then placed onto a heating mantle and the solvent evaporated off until a small amount of white solid was visible in the solution and a precipitate obtained. At this stage the heating was discontinued. After this step, the samples were left to cool down and then placed into a refrigerator at 4°C for 12 hours to favour further precipitation. The precipitated salt was separated from the supernatant by vacuum filtration and left to dry in a desiccator.



Scheme 1: Flow diagram for the production of Ammonium Perrhenate from CMSX-4 superalloy.

Scheme 1 illustrates the stages in the production of APR.

2.2 Instruments

Flame atomic absorbance analysis of the powder samples was performed on a Thermo Unicam 969 (Waltham, MA, USA). The spectrometer used a 37 mm single element rhenium hollow cathode lamp using a wavelength of 346.1 nm, lamp current of 75 mA and a band pass of 0.5 nm. The flame was generated using nitrous oxide and acetylene with a flow of 3.9 g/L and a flame stabilisation of 4. Calibration was performed using a 1000 ppm rhenium standard which was diluted to make standards of 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, and 50 mg/L. All samples and standards were made up using 15 MΩ deionised water.

For infrared analysis, a Perkin Elmer Spectrum 100 FT-IR Spectrometer (Waltham, MA, USA) fitted with a Specac- Standard Golden Gate ATR attachment was used. Ten milligrams of sample were placed on the ATR for analysis, which was performed at mid infra-red: 450-4000 cm^{-1} using 16 scans and a resolution of 4 cm^{-1} .

A Dionex ICS 1100 Ion Chromatograph (Waltham, MA, US) attached to an AS-DV auto sampler was used to analyse the samples for chlorides, nitrates and sulphates. Specification requirements were a 150mm column, a flow rate of 1 ml/min, an injection volume of 10 μl , and sample run times of 18 minutes for standards and 30 minutes for unknown samples. The eluent was 8.0mM sodium carbonate and the regenerant 2N sulphuric acid.

An FEI Inspect SEM attached to an INCAx-act EDX detector from Oxford Instruments (Abingdon, Oxfordshire, UK) using INCA Software was used for the analysis of metals in the powder.

Equilibrium analysis of the different metals in solution was performed with MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms software) (Ignasi Puig Domenec, Royal Institute of Technology, Stockholm, Sweden).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

The dissolution process of CMSX-4 is a complex process, and thermodynamics and kinetic properties of the ten different metals that constitute this alloy need to be considered. First, the selection of the dissolution agent is critical. Aqua regia will favour the highest oxidation states and will take the initial pH values below zero. Thermodynamic considerations for the process, and how they may affect the equilibrium for the different metals at the different pH values, will determine the species present in solution. Table 1 shows a summary of these species at different pH values using the model produced for each metal by MEDUSA software. Interactions between metals are not accounted for in the models.

Thermodynamic modelling shows that tungsten is oxidised to WO_3 , which is insoluble in a pH range from -1 to 2. A similar situation was observed for tantalum, which presented a solid phase of Ta_2O_5 at the pH used during the dissolution process. These insoluble complexes, coupled with incomplete leaching due to slow kinetics, explains why CMSX-4 was not fully dissolved following 5 hours of leaching in aqua regia. A gradual increase of the pH of the solution induced the precipitation of other metal species at different pH values (see Table 1) in such a way that, according to the thermodynamic models, at pH 13 only chromium and rhenium should remain in solution, provided other metals are filtered away as they form. ICP-OES (outsourced) analysis of a similar solution generated from aqua regia

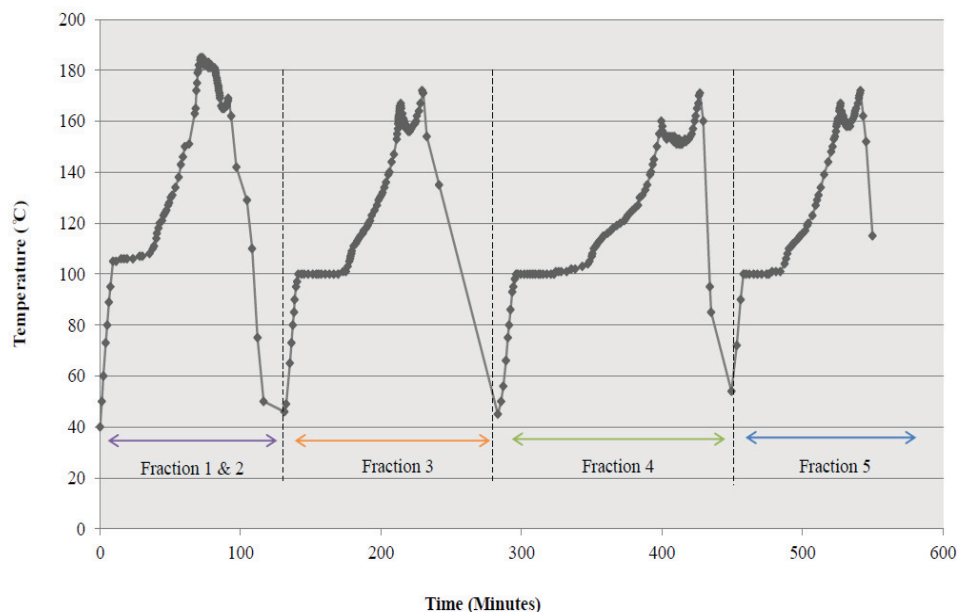


Figure 2: Distillation model for the purification process of APR.

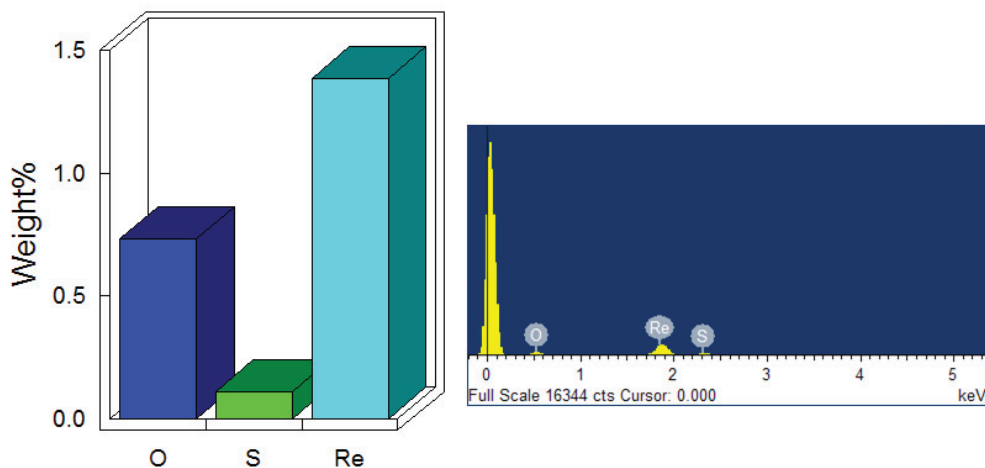


Figure 3: SEM-EDX analysis of the purest distillation fraction.

The final stage of the separation process, precipitation of ammonium perrhenate (APR), was performed by adding ammonia solution to the purest distillate (enriched perrhenic acid solution in fraction 4). The precipitation powder was analysed by SEM-EDX (figure 2), AAS and ion chromatography, and the results showed no other metals or contamination other than sulphates (data not shown).

The various options for the analysis of the powder produced at the end of the process were also a subject of this study. However, little information or research exists on the monitoring of rhenium in the extraction and

recycling from super alloys using molecular spectroscopic techniques, such as FTIR, in order to assess the purity of the products obtained in the process. Moreover, currently published research lacks discussion of contaminants from the refining process. Additionally, the non-destructive nature of FTIR, fast analysis time, and little or no requirement for sample preparation are obvious advantages of using a molecular spectroscopic method. Furthermore, this technique was also able to provide analysis of rhenium compounds at molecular level.

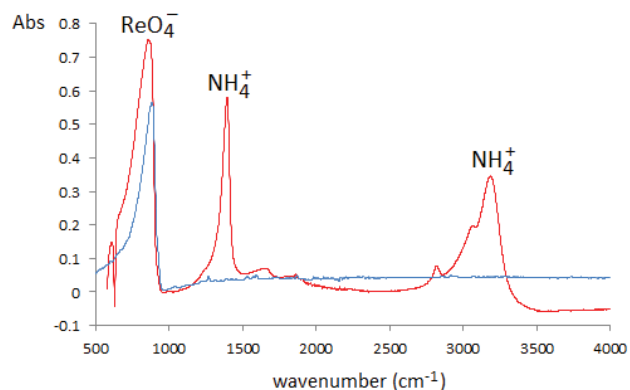


Figure 4: Ammonium perrhenate IR spectrum compared to potassium perrhenate spectra.

Hence, FTIR proved to be a convenient and effective method to allow for molecular identification, and it was a particularly powerful method alongside Atomic Absorption Spectroscopy (AAS), which provided the elemental analysis. AAS determined rhenium concentrations (mg/L) in the different unknown powders, whereas FTIR allowed for distinct chemical structure identification. In combination, these data, in comparison to known standards, permitted complete identification of components of a powder. This allowed for direct APR identification along with the ability to identify the various contaminants present in the sample, which AAS analysis alone could not provide.

The IR analysis of an ammonium perrhenate standard against a potassium perrhenate standard allowed for a greater understanding of the signal obtained from NH_4ReO_4 . The NH_4ReO_4 standard exhibited three peaks in the medium IR spectrum, whereas the KReO_4 standard only displayed one peak in the same IR range. The common peak obtained for the two standards corresponded to ReO_4^- ion (Figure 4). As potassium ion is IR transparent over the entire range of wavelengths, a peak for this ion would not be expected. Subsequently it can be deduced that the triple peak obtained in the wavelength range from 2783 to 3304 cm^{-1} and that at 1448 cm^{-1} are associated with the NH_4^+ ion [19] and the overlap peaks for both compounds at 913 cm^{-1} is related to the perrhenate (ReO_4^-) ion. The band obtained is very close to the band observed by Cao et al [17] at 910 cm^{-1} for ReO_4^- in the $[(\text{CuCl})_3\text{L}](\text{PF}_6)_2(\text{ReO}_4)_2 \cdot 3\text{H}_2\text{O}$ complex.

In FTIR, the peak intensity can be directly related to the concentration of the chemical species of interest, as IR spectroscopy follows the Beer-Lambert Law. For this, reason a range of APR standards at different concentrations were prepared to allow for the determination of peak intensities, and hence, when applied to the powders

Table 2: Analytical characteristics of the Infrared determination of APR and sulphates in the recycled samples.

Analytical parameters	ReO_4^- (913 cm^{-1})	SO_4^{2-} (1040 cm^{-1})
LoD (% w/w)	0.5	1.8
LoQ (% w/w)	1.5	2.3
R^2 calibration curve	0.9905	0.9837
Lineal range (%)	1.5-100	2.3-100
Repeatability (n=3)	10% w/w	6.6
RSD (%)	75% w/w	4.1
	10% w/w	99.6
Accuracy (%)	75% w/w	101.1
		96.1

produced, an estimation of APR concentration could be calculated. The same process was followed to evaluate the presence of sulphates in the powders, as this is the main contaminant likely to be present, as demonstrated by both SEM-EDX and ion chromatography analyses. A summary of the analytical characteristics of the method were produced and can be found in Table 2.

The determination of perrhenate allows for enhanced analysis as compared to sulphate complexes in the recycled matrix. The limits of detection and quantitation are also better for perrhenates than for sulphates. The linearity range is similar, and the method is suitable for the determination of main impurities found in the powder samples. If sulphates are present in very low concentrations, quantification is difficult. The precision and accuracy at higher concentrations for both ions are within acceptable limits. At lower concentrations the precision and accuracy for sulphates are not as good as for perrhenates but still within acceptable limits for a screening method. This was to be expected given that FTIR is not a particularly sensitive technique. Practically, these considerations are relatively unimportant to industrial applications, as the concentrations likely to be found for each of these compounds are much higher than those calculated for the LoD and LoQ. From the samples analysed after the recycling process, the amounts of sulphate and perrhenates found were always able to be assessed using spectroscopy, and results matched those obtained for atomic absorption or chromatography.

Figure 5 shows the correlation found between the responses obtained for AA analyses and FTIR for a set of 16 APR samples produced from the distillation process. It can be seen that, in general terms, both techniques can be considered statistically comparable as there is a distinct correlation between the two data sets. The experimental results obtained present a slope of 1.033 and an intercept

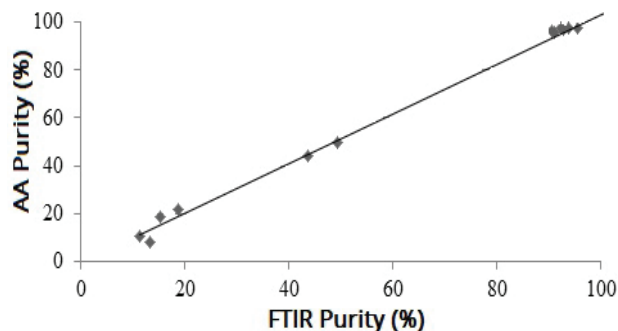


Figure 5: Correlation between FTIR and AA purity results.

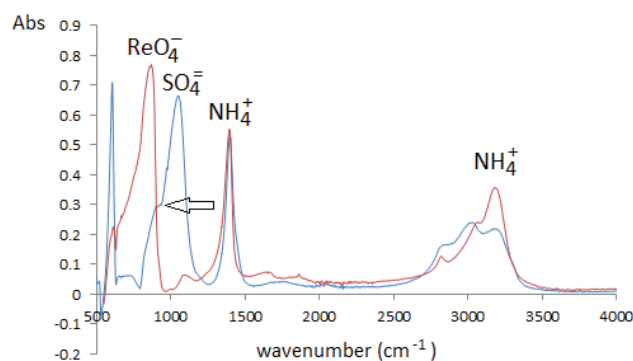


Figure 6: Two powder samples obtained from the purification process. Blue line: ReO_4^- (8.5%) and SO_4^{2-} (71.3%) and red line: ReO_4^- (92.4%) and SO_4^{2-} (6.9%).

of -0.342 with a correlation coefficient of $R^2=0.991$. As the slope is close to 1 and the intercept is close enough to zero we can establish that there is a close relationship between the values for AAS and FTIR as there is also a good correlation.

In order to identify and determine APR in complex mixtures, the determination of potential contaminants was performed in the recycled powder to assess the robustness of the method. A range of samples obtained following the recycling procedure were analysed using ion chromatography for the presence of nitrates, chlorides and sulphates, as these were the typical contaminants likely to be found in the recycled powders, and the purity of rhenium (as %Re) was calculated using AA. Figure 6 shows an example results from two very different samples in which the concentrations of rhenium and sulphate were 18.5% and 71.3%, respectively, for the first sample and 92.4% and 6.9% for the second sample. It was also noticed that, in general, an increasing concentration of sulphates and contaminants had the ability to shift the perrhenate peak towards longer wavenumbers. In this way,

a concentration of 6.9% in sulphate concentration would allow the perrhenate peak to be measured at 871 cm^{-1} , while a highly contaminated sample with a concentration of sulphates of 71.3% would shift the perrhenate peak to 915 cm^{-1} , showing it as a shoulder on the slope of the sulphate peak (indicated by the arrow in Figure 6). These cases were also considered and included in the estimation of the experimental error of the method. The shifting of the perrhenate peak did not particularly affect the ability of this method to identify the different species or to calculate accurate concentrations. In some particular cases, where a very small amount of nitrates were found in the powders, the peak appeared at 1400 cm^{-1} , which is far from those of sulphates or perrhenates. Given this result, nitrates are not considered an interference for perrhenate or sulphate quantification. Chlorides are transparent in infrared spectroscopy and also not a problem for the determination of rhenium.

Table 3 displays a typical example of data obtained from the distillation process. Ion chromatography confirmed that no nitrates were found and only small amounts of chlorides were present in these two powder samples. For this case, fractions 3 and 4 were found to have sulphate contaminations of 6.92% and 6.87%, respectively. Accordingly, it can be argued that FTIR can be used as a technique to provide information on the rhenium content but also to aid in the identification of contaminants within the powders as the peaks for sulphates and rhenium were identified and concentrations accurately calculated.

4 Conclusions

The separation and monitoring of the different stages of a recycling process to extract rhenium from a CMSX-4 superalloy and produce ammonium perrhenate (APR) were performed. The identification and quantitation of this anion and main contaminants present from the extraction process were performed by Atomic Absorption Spectroscopy (AAS), Fourier transform infra-red spectroscopy (FTIR), Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) and ion chromatography (IC). AAS allowed for elemental identification and quantitation of the rhenium present in the sample, whereas FTIR provided the crucial aspect of molecular identification to determine whether APR was effectively produced. Using ion chromatography, SEM-EDX and AAS, some of the main contaminants present in the final product were also identified and quantitated. FTIR also succeeded in monitoring the most important

Table 3: Ion chromatography results for an example distillation result for fractions 3 and 4.

Distillation	Purity of APR	Chloride %	Nitrate %	Sulphate %
Distillation: Fraction 3	92.83±1.32 %	0.55±0.03	0.00	6.92±0.09
Distillation: Fraction 4	92.39±1.78 %	0.54±0.05	0.00	6.87±0.08

contaminants both qualitatively and quantitatively. These were identified to be nitrates, chlorides and sulphates coming from the different acids used in the separation process. No other metals but rhenium were found in the APR samples obtained from the recycling process. Samples obtained from the CMSX-4 superalloy were then successfully recycled and analysed, opening an interesting door for the re-utilisation of this scarce metal.

To the best of our knowledge, no research is available in the literature on the analysis of APR by FTIR spectroscopy with the aim of identification and quantitation of this anion from CMSX-4 superalloy extracts. From an analytical point of view the characteristics for an infrared method to identify perrhenate anions extracted from CMSX-4 have been presented and a comparison with the atomic absorption method used, as a reference standard demonstrated that there are no statistically significant differences between the two methods. Subsequently, it has been established that although atomic absorption spectroscopy continues to provide useful elemental information, FTIR spectroscopy can provide considerably fast quantitative and qualitative analysis in the recycling process of the superalloy CMSX-4.

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Conflict of interest: Authors declare no conflict of interest.

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