

RECOVERY OF PLATINUM GROUP METALS FROM SECONDARY SOURCES BY SELECTIVE CHLORINATION FROM MOLTEN SALT MEDIA

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Keywords: platinum group metals, PGM, molten chlorides, selective chlorination, secondary resources, spent catalyst, recycling

Abstract. The use of molten salts as "solvents" offers interesting possibilities for the treatment of ores, industrial by-products as well as scraps, allowing the development of processes that are mid-way between pyro- and hydrometallurgy, with the advantage of salts offering a wide choice of chemical and electrochemical properties. The molten mixtures can be fed to industrial electrolytic cells (electrometallurgy) where the reactions can take place. One example of this type of reactions is the selective chlorination using gaseous mixtures in a molten chloride salt mixture. Within the frame of the EU-financed project PLATIRUS (GA 730224), the possibility of selective chlorination of platinum group metals (PGM) contained in spent automobile catalyst samples, using a molten salt as reaction media was investigated. To predict the selective separating conditions of the PGMs from the sample matrix, the Pourbaix type E-pO²⁻ diagrams of the most relevant components in the spent catalyst were compared with those of relevant chlorinating gaseous mixtures, i.e. Cl₂/O₂. This allowed to predict the optimal chlorinating conditions, which were tested and confirmed experimentally using Cl₂ gas.

1. Introduction

Platinum group metals (PGM) are among the least abundant elements in the Earth's crust and they are classified as critical raw materials (CRMs). They have large range of applications from jewelry to automotive and electronics. Considering autocatalysts only, Europe is the world's largest consumer of PGMs, with an annual demand of 40 tons of platinum, worth 1137 MEUR [1].

The supply of PGMs is currently ensured mostly by primary sources (72%) and the overall supplied PGMs, that comes from both mines and recycled products cannot meet the global demand. Then, the recycling of secondary resources must be promoted to tackle sustainability challenges associated with PGMs. If 100% of the PGM available in end-of-life autocatalysts is recovered, an additional 29 tons of PGM will become available in the global market, which is about 1.5 times of the global supply-demand gap [2].

Within the frame of the EU-financed project PLATIRUS (GA 730224), SINTEF has investigated the possibility of recovering PGM from spent automobile catalysts by selective chlorination from a molten salt.

The use of molten salts as "solvents" offer interesting possibilities for the treatment of ores, industrial by-products as well as scrap. By using salts in the temperature range of 200-500 °C, it is possible to develop processes that are mid-way between pyro- and hydrometallurgy, with the advantage of salts offering a wide choice of chemical and electrochemical properties. One example of this type of reactions is the selective chlorination using gaseous mixtures in a molten chloride salt mixture.

Chlorination of metallic oxide mixtures (or even ores or industrial by-products) in molten chlorides media can take place at moderate temperatures, leading to the selective separation of different compounds by choosing the appropriate conditions (salt, temperature, chlorinating agent, etc.). The dissolution reaction is favored by significant solvation of the oxide ion (O²⁻) and the produced metal cation (Mⁿ⁺) giving stable complexes with the anions (Cl⁻) of the solvent. This is a considerable advantage compared with classical gas-solid reaction systems using solid reductants (i.e., carbo-chlorination), where the rate and conversion levels are limited by the intimate contact of the reductant and the metal oxide particles, and the reaction is occurring non-selectively at much higher working temperatures (ca. 1000 °C).

Selective separation conditions of the PGMs from the spent catalyst matrix were predicted by comparing the Pourbaix type E-pO²⁻ predominance diagrams of the most relevant components in the material with those of the utilized chlorinating gaseous mixture. The most promising conditions were tested and confirmed experimentally using Cl₂ gas in two molten salt media with different oxoacidic properties, namely the eutectic LiCl-KCl mixture and the equimolar CaCl₂-NaCl melt. The effect of the working temperature in the chlorination process was also studied, and the PGM recovery rates were assessed in each case. The results allow to establish the optimal operating conditions for the recovery of PGMs from spent automobile catalyst waste.

Molten Salts as Reaction Media

Molten salts are ionized solvents that, as any other liquid solvent (aqueous or non-aqueous), can dissolve substances and make them react with one another, following reactions in solution at high temperature.

Chemical reactions in liquid media at high temperatures offers two main advantages: i) Reactions kinetics are more enhanced than at ambient temperature and nearly always obey the laws of chemical equilibrium; ii) The reactions can be controlled, as the temperature can be easily controlled, then reaction selectivity is as large as those offered in other liquid solvents.

The structure of the molten salt is looser and more disordered than in the crystalline state, thus allowing high solubility (complete miscibility) of the solute added, which is subjected to the phenomenon of solvation by the species of the molten salt used as solvent. The solvation involves interactions of the electrostatic type (Coulombic) and, frequently, cation-anion coordination. The differences in the solvation state have the most important consequence of modification of reactivity.

The O²⁻ Anion. Acidity in Molten Salts

The oxide anion, O²⁻, frequently exists in the free state, i.e., without the interaction of solvation other than the Coulombic interaction with the surrounding ions of the molten salt.

The O²⁻ ion plays a particularly important role in molten salts, which arises from the natural abundance of compounds that contain it, constituting the major part of mineral resources. On the other hand, the O²⁻ ion is the most remarkable base (electron pair donor), capable of combining with all acceptors of electron pairs (Lewis acid), and particularly, metallic cations. It is then possible to develop a system of reactions in molten salt solvents involving the oxide ion O²⁻ following the acid-base concept, as in analogy with the case of the H⁺ ion in water and other molecular solvents [3,4], as in **Error! Reference source not found..** The level of oxoacidity in a molten salt can be measured by the pO²⁻ value, analogous to pH and playing the same role, as defined in **Error! Reference source not found..**



$$p\text{O}^{2-} = -\log a_{(\text{O}^{2-})} = \log m_{(\text{O}^{2-})} \quad \text{Reaction 2}$$

The E-pO²⁻ Diagrams

The E-pO²⁻ diagrams in molten salts are like the E-pH diagrams (Pourbaix diagrams) in aqueous systems. They represent the variation of the equilibrium potentials of the Red-Ox systems as a function of pO²⁻, at fixed concentrations of the oxidizing and reducing substances.

In the case of molten alkaline chloride solvents, the higher value of E corresponds to the oxidation of Cl⁻ ions to chlorine, at a partial pressure that, in ordinary conditions, does not exceed 1 atm. The higher value corresponds to the normal chlorine electrode (NCE) taken as reference electrode, with E=0 by convention. On the other hand, the lower E value corresponds to the alkaline metal, which can be determined by thermochemical tabulated data with respect to the NCE at the given temperature.

Concerning the pO²⁻ values, the only theoretical limit is imposed by the solubility of the alkali oxide.

Solubilization Conditions of Insoluble Metallic Oxides

The solubilization of an insoluble oxide (MO) in a molten salt solvent, needs the establishment of a sufficiently high pO²⁻ in the molten salt. This can be obtained either by the addition of a strong enough oxoacid reactant, which will combine with the O²⁻ anion giving the conjugated oxobase, or by the oxidation of the O²⁻ into oxygen by the addition of a sufficiently strong oxidizing reactant, like chlorine gas. Maximum efficiency can be obtained when these two actions are combined.

In the case of molten chloride solvents, the insoluble oxides are converted to soluble chlorides, and this solubilization process (dissolution or vaporization) is often called chlorination, which can be selective by choosing the appropriate conditions, i.e., pO²⁻ value, and then separations of metallic oxide mixtures can take place.

The chlorination conditions can be predicted by comparing the E-pO²⁻ predominance diagrams of the M-O-Cl substances with that of the chlorinating agent, in the molten chloride at the operating temperature. When the zone of the gaseous mixture covers an insoluble oxide, the reactant does not have a solubilizing action. In the contrary, when a zone covers a chloride (soluble or volatile) salt, it indicates that the reactant has a chlorinating action. Comparing several elements indicates if these actions can be selective.

2. Experimental

Experimental set-up

90 g of a molten salt mixture (eutectic LiCl-KCl or equimolar CaCl₂-NaCl) was mixed with 10 g of spent catalyst powder in a quartz crucible, which was placed in a quartz cell under inert atmosphere (Ar 99.999%) with a water-cooled quartz lid that allowed the insertion of a thermocouple, and gas and sampling tubes. The glass reactor was placed in a vertical furnace with a mullite liner.

All salts and the catalyst waste material were dried at 200 and 100 °C, respectively, for at least 48 h prior to use. The working temperature was measured using a thermocouple type S (Pt-Pt 10 %Rh) shielded by a closed-end alumina or quartz tube. The temperature was monitored continuously by means of a multichannel Keithley 2000 Multimeter.

Samples of the molten bath were taken prior to and after the chlorination experiments, using a quartz tube with a quartz frit to avoid solid particles. The samples were cooled-down in a desiccator and there stored until analyzed by ICP-SFMS (Inductively Coupled Plasma Sector Field Mass Spectrometry).

After the chlorination trial, the furnace was cooled down under argon to room temperature, and the next day the cell was opened and investigated.

The furnace, gas system, valves, gas control panel, electronic mass flow controllers-control system, pressure gauge and transmitter and pressure relieve valve are schematically shown in Figure 1. The complete equipment was installed in a walk-in hood and only materials and apparatus able to stand high temperature and chlorine atmosphere were used, i.e., glass, special valves, and mass flow controllers (MFC), pressure gauges, etc.

To absorb the unreacted chlorine gas coming from the cell, 6M sodium hydroxide solutions in gas washing bottles were placed in the gas outlet. This proved to be a very efficient scrubber, and as long as the sodium hydroxide was not saturated, no chlorine gas passed these bottles. Also, a liquid N₂ (LN2) cooling trap was positioned at the end of the gas line to account for safety if volatile chlorides were released from the reactor. A U-tube was connected in parallel with the gas outlet to ensure an alternative escape route for the off gas in case of clogging of the NaOH scrubbers or LN2 trap to prevent pressure build up in the reactor.

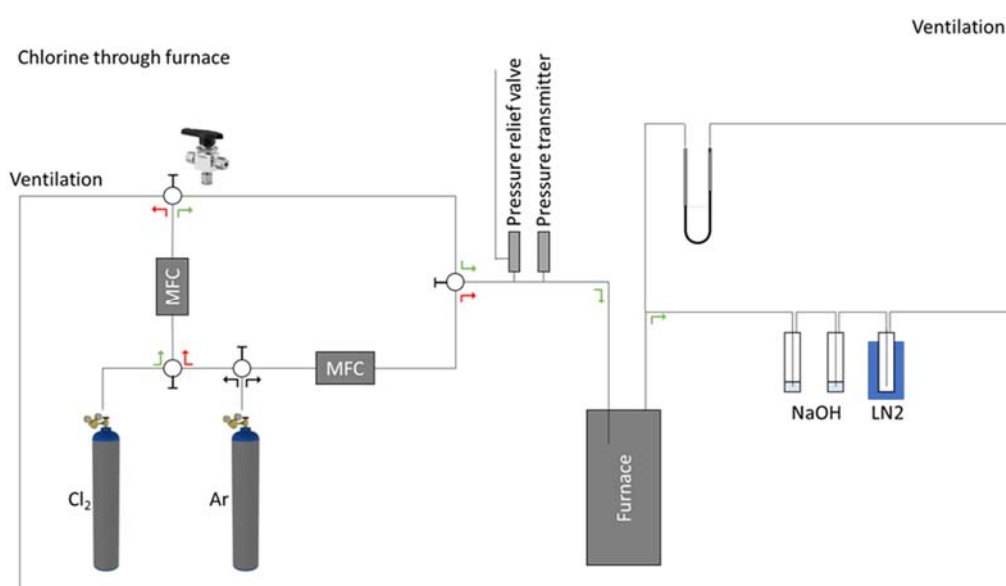


Figure 1. Schematics of the chlorination apparatus

Methodology

The reactor was kept completely gas tight when it was under chlorine gas atmosphere. When the set temperature was obtained, still under argon addition, the gas inlet tube was lowered into the melt. The gas was then switched to chlorine via the gas control panel so that chlorine gas was bubbled directly into the molten salt. The flow of Cl₂ gas was 100 ml min⁻¹, which corresponds to ca. 17.5 g h⁻¹. This value was chosen following the data from the literature [5]. When the chlorination was finished, argon gas was introduced to strip the melt of chlorine and remove the chlorine from the gas line before opening the cell for further manipulation, i.e., taking melt samples, etc.

Samples of the molten bath were taken prior to and after each of the chlorination tests, using a quartz tube with a quartz frit to avoid solid particles. The samples were cooled-down in a desiccator and there stored until analyzed by ICP-MS/OES (Inductively Coupled Plasma Mass Spectrometry/Optical Emission Spectrometry).

Once the experiment was finished, the furnace was cooled down under argon to room temperature, and the next day the cell was opened and investigated. The catalyst material left at the bottom of the reactor was recovered, after washing the entrapped salt with water, and then analyzed by ICP-MS/OES.

3. Results and Discussion

Choice of the Molten Salt Media

The most attractive molten salt media are the molten halides, as there is no limitation of high pO_2 , and particularly molten chlorides, where the insoluble oxides are converted to soluble chlorides.

In general, molten chlorides are not recommended to be used at working temperatures higher than 850-900 °C, due to the high vapor pressures at those temperatures, leading to large vaporization loss of the reaction media.

The most common molten chloride media are the eutectic LiCl-KCl molten mixture, and the equimolar NaCl-KCl mixture. Both have been widely studied, and many data on the chemical and electrochemical properties of metallic elements in those media can be found in the literature. Moreover, their oxoacidic properties are also well known [e.g.6,7].

The eutectic mixture LiCl-KCl is very attractive, due to its low melting point (ca. 348 °C), thus allowing a wide range of working temperatures, going from relatively low, i.e., 400 °C, to relatively high, i.e., 800 °C. The equimolar mixture NaCl-KCl has a higher melting point (ca. 645 °C), thus 727 °C (1000 K) is the standard temperature used in this type of molten salt.

Another attractive and well-studied molten chloride is the eutectic $CaCl_2$ -NaCl, of composition close to that of the equimolar mixture. The melting temperature is ca. 500 °C, thus 550 °C is the usual working temperature used in the literature. The equimolar $CaCl_2$ -NaCl mixture possess a higher oxoacidity than the above-mentioned molten chlorides [8], thus affecting the O^{2-} exchange reactions and the solvation effect of the metallic ions. In addition, it is known that PGMs are easily forming complexes with Ca^{2+} ions, thus perhaps influencing the solubilization reactions of PGMs in $CaCl_2$ -based media.

The eutectic LiCl-KCl and equimolar $CaCl_2$ -NaCl mixtures were used in the chlorination tests. The effect of temperature in the chlorination kinetics was also studied in both cases.

Characterization of the Raw Material

The spent catalyst material was provided in the form of fine particles by Monolithos Catalysts Ltd [9]. X-ray diffraction (XRD) analysis of the particles showed that it consists mainly of SiO_2 , Al_2O_3 and MgO (indialite/cordierite ceramic monolith). Some hydroxide phases as well as silicon were also found (cf. Figure 2). Quantification of the different phases was done using Bruker TOPAS Software, being Indialite: 73.09%; Cordierite: 17.44%; magnesium silicon oxide hydroxide hydrate: 4.56%; and silicon: 4.92%.

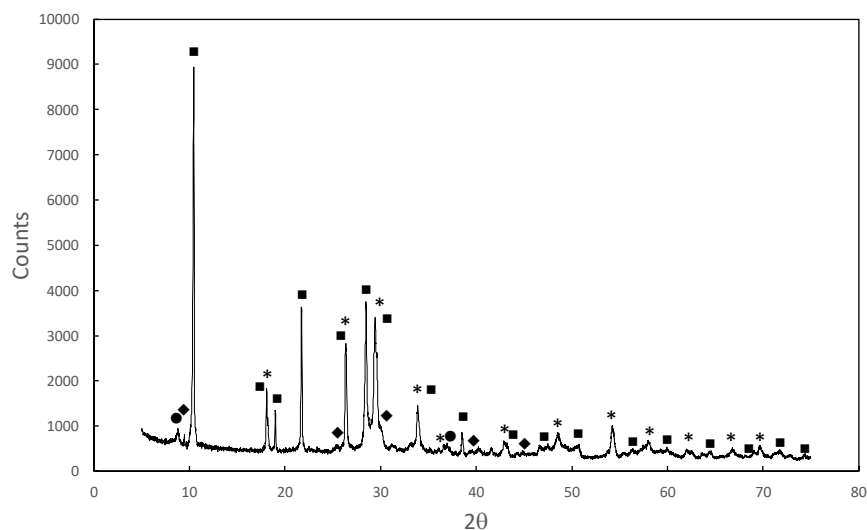


Figure 2. XRD diffractogram of the spent catalyst sample. (*) $Mg_2(Al_4Si_5O_{18})$ Indialite; (■) $Mg_2Al_4Si_5O_{18}$ Cordierite; (●) $Mg_3Si_4O_{10}(OH)_2(H_2O)$; (◆) $Na_{3.7}Al_{3.7}Si_{8.3}O_{24}(H_2O)_{11}$.

ICP-MS/OES analysis of the catalyst sample is shown in Table 1. The material has a total PGM content of ca. 2500 ppm.

Table 1. Elemental composition of the spent catalyst material analyzed by ICP-OES. The PGM content is analyzed by ICP-MS.

Pd	Pt	Rh	Al	Si	Mg	Zr	Ce	Ba	Ca	Fe	La	Pb	Ti	Zn
ppm	ppm	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1453	819	279	20.0	17.9	5.8	2.7	4.4	8011	4337	7699	6848	1969	7055	2667

Chlorination in the Eutectic LiCl-KCl Mixture

The E-pO²⁻ diagrams of the most relevant elements present in the waste catalyst material (Si, Al, and Mg) in the eutectic LiCl-KCl mixture are available in the literature [10,11]. Their comparison with that of the Cl₂/O₂ mixture, is also available in the literature [12]. This information enables predicting the solubilization conditions of the different elements, either by dissolution as chloride complexes, or by vaporization.

Even though chlorine possesses the strongest oxidizing capacity in molten chlorides, this reactant is not capable of solubilizing the most stable metallic oxides. Also, it is expected that SiO₂ cannot be chlorinated at the experimental conditions, most likely remaining as insoluble silicates. Al and Mg could be easily chlorinated as AlO⁺ and Mg(II) complexes, if kinetics of the chlorination reaction are high enough.

Moreover, the theoretical regions of the PGM-O-Cl compounds as a function of the partial pressures of Cl₂ and O₂ gases could be determined from thermodynamic data (cf. Figure 3). The thermodynamic data show that all PGMs can be chlorinated with pure chlorine and that Rh-O compounds are very stable even at low oxygen partial pressures. However, the solvation effect of the chloride complexes in the molten salt (activity) must also be considered.

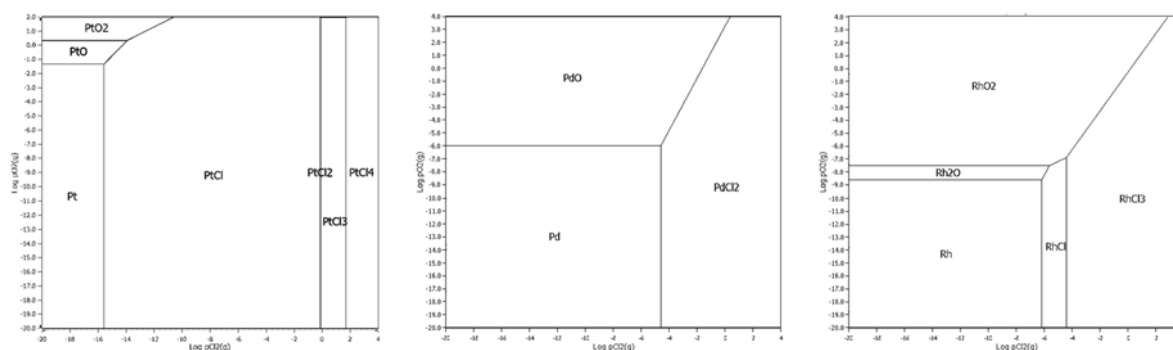


Figure 3. Theoretical stability regions of the PGM-O-Cl compounds as a function of the partial pressures of Cl₂ and O₂ gases. Temperature 450 °C. Data obtained from HSC Data Base.

In order to confirm the theoretical predictions, chlorination experiments were carried out using chlorine gas at two different working temperatures, i.e., 450 and 750 °C, and at different chlorination times, i.e., 1, 2, 3, and 5 h.

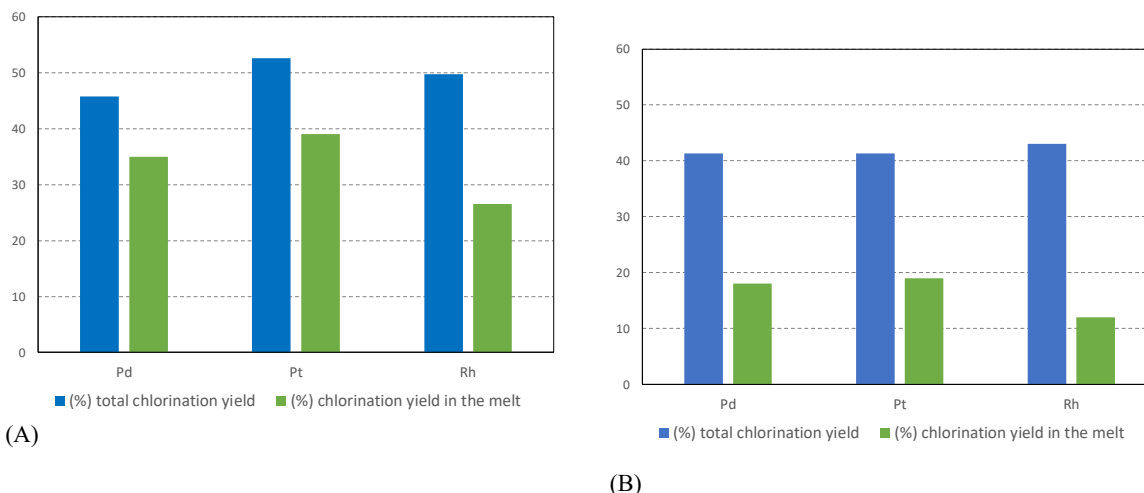
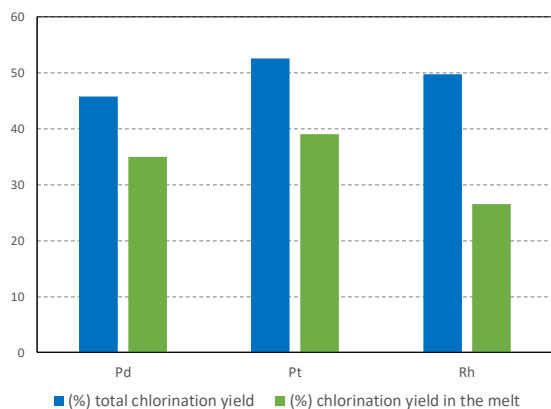
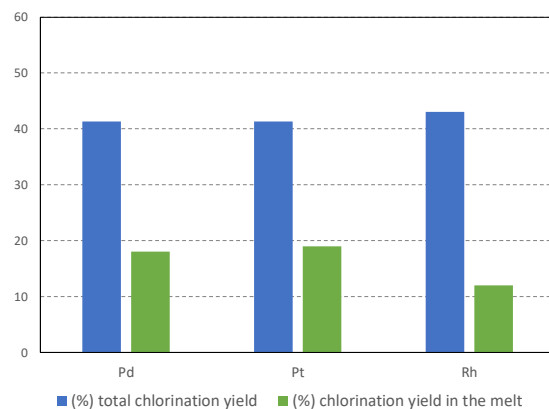


Figure 4 shows the total chlorination yield of PGMs, which was calculated by analyzing the remaining catalyst sample after the chlorination runs compared with the initial PGM content in the waste catalyst material, as a function of temperature. The chlorination yield in the melt was determined by analysis of the melt samples. Indirectly the amount of PGM chloro-complexes lost in the vapor phase can also be extracted from the results obtained. The results showed that increasing the working temperature did not affect the total chlorination yield, but only the content of PGM in the vapor phase.



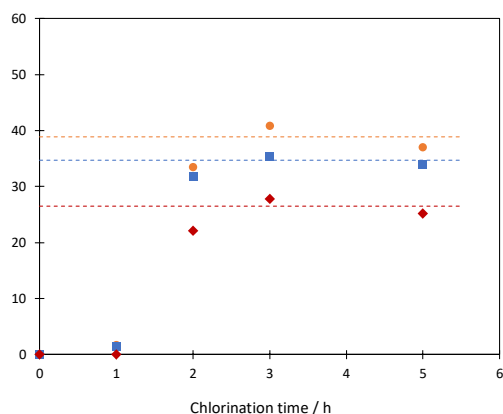
(A)



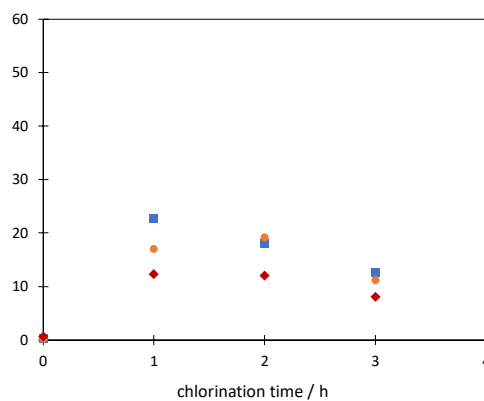
(B)

Figure 4. PGM content in the remaining catalyst material and in the molten salt samples after the chlorination runs in the eutectic LiCl-KCl mixture at two different working temperatures: (A) 450 °C; and (B) 750 °C.

Moreover,

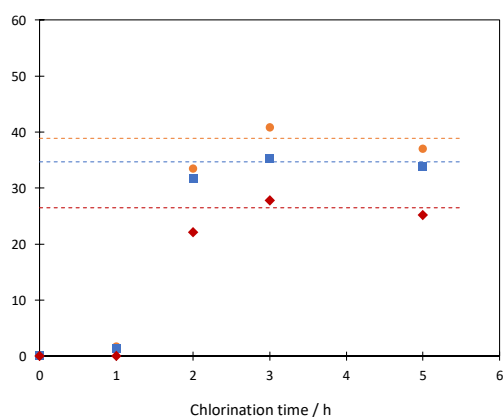


(A)

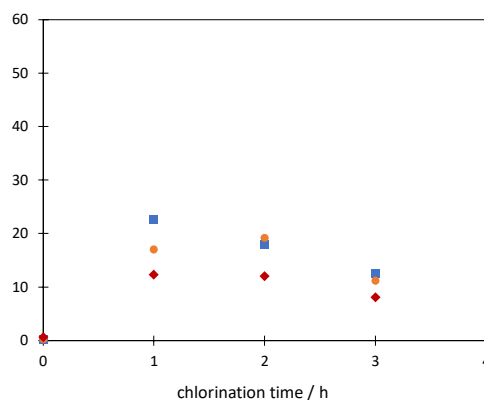


(B)

Figure 5 shows the amount of PGMs in the molten salt as a function of the chlorination time. At lower temperatures, it was found that after 2-3 h chlorination time, the amount of PGM oxo-complexes in the molten bath is constant. In the case of high working temperatures, the effect of the elapsed time in the losses of the dissolved PGM-chloride complexes by evaporation is clear.



(A)



(B)

Figure 5. PGM yield in melt (%) in the eutectic LiCl-KCl melt as a function of the chlorination time at (A) 450 °C; and (B) 750 °C. (●) Pt; (■) Pd; and (◆) Rh.

The results obtained for other elements are shown in Figure 6. In the case of the metallic elements from the main phase indialite/corderite, i.e., Al, Mg, and Si, the results showed that they remained in the catalyst material after chlorination, most likely as silicates, which are not possible to solubilize using chlorine gas at the working conditions.

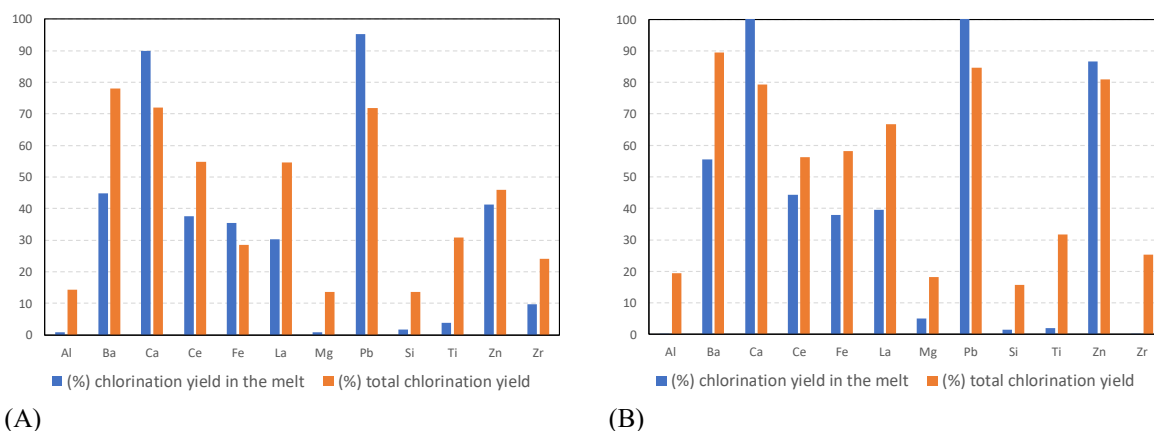
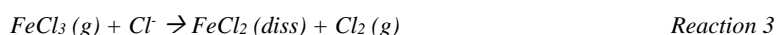
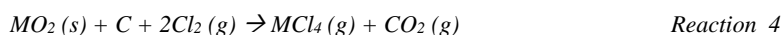


Figure 6. Element analysis of the remaining catalyst material and molten salt samples after the chlorination runs in the eutectic LiCl-KCl mixture at two different working temperatures: (A) 450 °C; and (B) 750 °C

Lanthanides (La and Ce), alkaline earth (Ca, and Ba) and base metals (Zn, Pb, Fe) are chlorinated and remain in the molten bath, in some cases with an efficiency up to almost 80-100%, as in the case of Ca, Ba, Pb, Zn at 750 °C. At the operating conditions, the gaseous FeCl₃ formed during the chlorination reaction and reacted with the chloride ions of the molten bath, resulting in stable Fe(II) species dissolved in the melt, according to Reaction 3:



Surprisingly, total chlorination yields of Zr and Ti reached 20-30 %. This is probably due to the fact that the catalyst waste material contained some carbon acting as auxiliary reductant, thus it underwent a carbo-chlorination reaction in which higher pO₂ values can be achieved [14,15], and then gaseous TiCl₄ and ZrCl₄ formed according to **Error! Reference source not found.** This was confirmed by the fact that, especially at the higher temperatures, i.e., 750 °C, both elements were found in the vapor phase. However, a reaction similar to **Error! Reference source not found.** cannot be ruled out, explaining the small amounts of dissolved Zr- and Ti-chloro complexes obtained in the bath samples at lower temperatures.



Under these conditions, it is possible to predict the separation of the PGMs from other metal-chlorocomplexes dissolved in the molten LiCl-KCl by electrolysis, due to the differences in standard potentials of the elements involved (cf. Table 2). It seems to be difficult to separate the different PGMs by electrochemical methods, due to their similar standard potential. However, a PGM alloy could be selectively separated from the rest of the dissolved species present in the electrolyte.

Table 2. Theoretical standard potentials of the reduction systems of relevant elements dissolved in the molten chloride, including the matrix (eutectic LiCl-KCl melt). Temperature 450 °C.

Reduction reactions	E° / V vs Cl ₂ /Cl ⁻ ref.
PtCl ₄ (s) + 4e ⁻ = Pt (s) + 4Cl ⁻	-0.212
PdCl ₂ (s) + 2e ⁻ = Pd (s) + 2Cl ⁻	-0.328
RhCl ₃ (s) + 3e ⁻ = Rh(s) + 3Cl ⁻	-0.357
RhCl ₂ (s) + 2e ⁻ = Rh (s) + 2Cl ⁻	-0.369
PtCl ₂ (s) + 2e ⁻ = Pt (s) + 2Cl ⁻	-0.404
FeCl ₂ (s) + 2e ⁻ = Fe (s) + 2Cl ⁻	-1.292
PbCl ₂ (s) + 2e ⁻ = Pb (l) + 2Cl ⁻	-1.308
ZnCl ₂ (s) + 2e ⁻ = Zn (l) + 2Cl ⁻	-1.595
CeCl ₃ (s) + 3e ⁻ = Ce (s) + 3Cl ⁻	-3.016
LaCl ₃ (s) + 3e ⁻ = La (s) + 3Cl ⁻	-3.083
CaCl ₂ (s) + 2e ⁻ = Ca (l) + 2Cl ⁻	-3.567
LiCl (s) + e ⁻ = Li (l) + Cl ⁻	-3.680

$\text{BaCl}_2 (\text{s}) + 2\text{e}^- = \text{Ba} (\text{l}) + 2\text{Cl}^-$	-3.848
$\text{KCl} (\text{s}) + \text{e}^- = \text{K} (\text{l}) + \text{Cl}^-$	-3.878

Chlorination in the Equimolar $\text{CaCl}_2\text{-NaCl}$ Melt

In this case, chlorination experiments were carried out at two different working temperatures, i.e., 550 and 790 °C, and at different chlorination times, consecutively during the same run. Figure 7

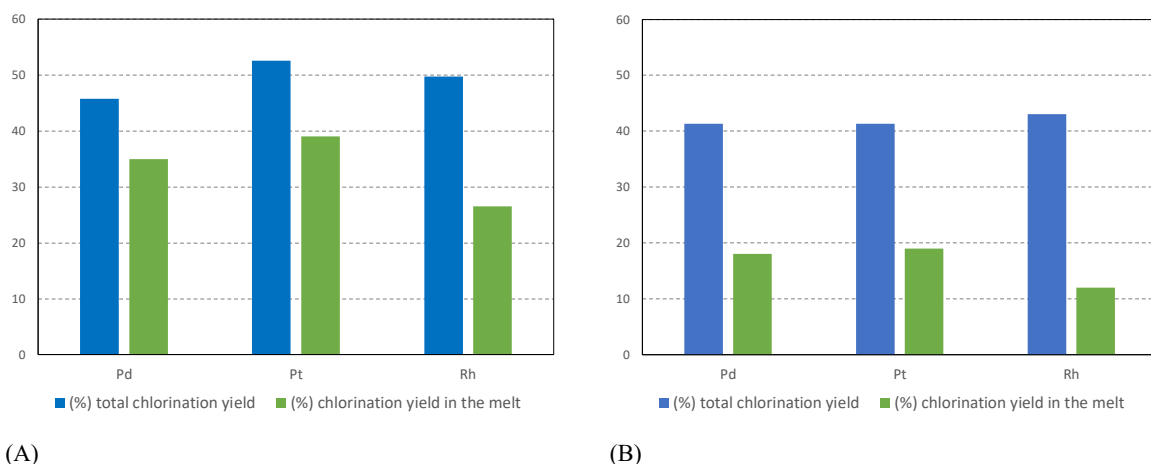


Figure 4 presents the ICP-MS analysis results of molten salt samples taken during the test.

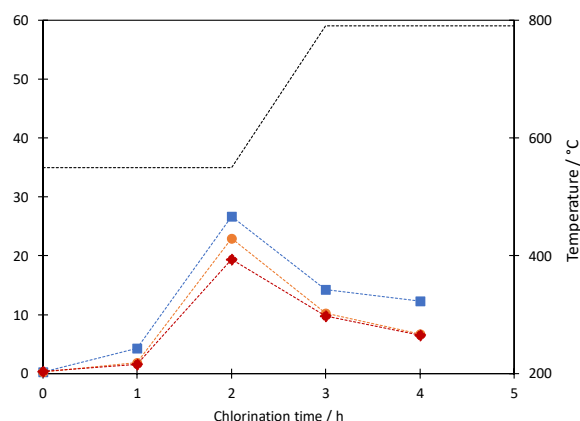


Figure 7. PGM yield in the melt (%) in the equimolar $\text{CaCl}_2\text{-NaCl}$ mixture as a function of the chlorination time and at the working temperature showed by the broken line, i.e., 550 °C and 790 °C. (●) Pt; (■) Pd; and (◆) Rh. The x axes do not reflect the real elapsed time during the test.

As in the case of the LiCl-KCl melt, the effect of the elapsed time in the loss of the dissolved PGM-chloride complexes by evaporation is clear at higher temperatures. The rest of the elements showed a similar behavior, except for the lanthanide elements, i.e., Ce and La, that gave chlorination yields in melt close to 70% at the higher working temperature of 790 °C.

4. Summary and concluding remarks

The possibility of selective chlorination of PGMs contained in spent automobile catalyst samples, using a molten salt as reaction media was investigated. The selective separating conditions of the PGMs from the spent catalyst matrix were estimated by comparing the Pourbaix type E-pO^{2-} predominance diagrams of the most relevant components in the material with those of the utilized chlorinating gaseous mixture. The most promising conditions were tested and confirmed experimentally that using Cl_2 gas in two molten salt media with different oxoacidic properties, namely the eutectic LiCl-KCl mixture and the equimolar $\text{CaCl}_2\text{-NaCl}$ melt is possible. The effect of the working temperature in the chlorination process was also studied, and the PGM recovery rates was assessed in each case.

Similar results were obtained in both melts, and chlorination yields of the PGMs were found to be 40-50% after 2-3 h of passing chlorine gas through the molten salt at 100 ml min^{-1} , i.e., ca. 17.5 g h^{-1} . Increasing the working temperature did not lead to better chlorination yields, but the evaporation losses were significantly higher.

Elemental analysis of the remaining catalyst material as well as that's of the salt samples taken during the chlorination runs, allowed to determine the elements dissolved in the molten chloride as chloro-complexes. Lanthanides (La and Ce), alkaline earth (Ca, and Ba) and base metals (Zn, Pb, Fe) are chlorinated in some cases with an efficiency of up to almost 80-100%, as for Ca, Ba, Pb, Zn at the higher working temperatures.

It was also found some extent of carbo-chlorination reaction, due to small amounts of carbon existing in the waste catalyst material. This explains the certain chlorination of Ti and Zr, which were found to escape in the vapor phase as gaseous TiCl_4 and ZrCl_4 .

The results of this study show that the most suitable molten chloride system is the eutectic LiCl-KCl melt, allowing working at relatively low temperature of $450 \text{ }^\circ\text{C}$. Under these conditions, the PGMs can be selectively recovered from the waste catalyst material by chlorination and subsequent electrolysis from the same molten chloride acting as an electrolyte.

Acknowledgements

Zhaohui Wang is acknowledged for performing XRD/TOPAS analysis, Tecnalia Research and Innovation for the ICP-MS/OES analysis of the catalyst sample and Kai Tang for providing thermodynamic data of PGM-Cl-O compounds. This work has received funding from the European Union's H2020 Programme under GA No. 730224 (www.platirus.eu).

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