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Late transition metals recovery from silver nitrate electrolyte using a phosphine-oxide bearing scavenger

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Electronic Supplementary Information—Calorimetric study of MPX-310 resin in silver electrolyte from electrorefining process

The experiments performed by Innovhub were performed with an Accelerating Rate Calorimeter (ARC), an adiabatic calorimeter produced by Columbia Scientific Industries (Texas, USA). The ARC allows to determine the thermal behavior of the mixture, the onset temperature, the time induction (TMR), the rate of change in temperature and pressure and to characterize the analyzed system (to determine if the produced gases are non-condensable). The ARC is the most commonly used adiabatic equipment for thermal runaway detection. The equipment used for the safety experiments is presented in Figure 1.

Figure 1. The ARC adiabatic calorimeters used to perform safety experiments using Magpie resins and silver electrolyte effluents.

The ARC device consists of a spherical sample holder build of stainless steel or Hastelloy C of about 10 cm^3, placed in an insulated vessel, a radiant heater, which raises sample temperature up to the set value, a thermocouple connected to the sample holder wall and used to record the sample temperature, an insulated jacket with thermocouples and heaters to maintain the oven temperature equal to the temperature of the sample, in order to guarantee the adiabaticity of the cell and a capillary tube that links the sample holder to a pressure transducer. The scheme of this type of calorimeter is presented in Figure 2.

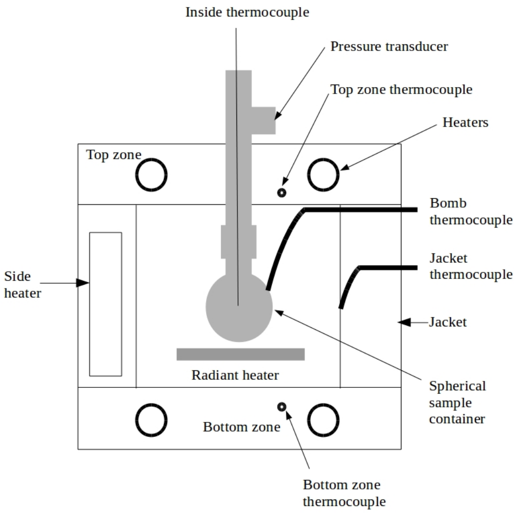


Figure 2. Working principle for an ARC calorimeter(Townsend and Tou, 1980)

Time, temperature, and pressure data are recorded at specified temperature intervals as a function of time. The recorded data is used to calculate the time rates of changes in pressure and temperature. These data can also be used to calculate a time-to-maximum rate. Runaway detection is very good, and a low onset temperature is detected (sensitivity can be down to 0.02°C/min), but the Φ-factor values prohibit the use of data directly for vent sizing. Experiments can be set in three different modes: ramp, heat-wait-search (HWS) or isoaging.

The experiments set in the ARC followed the HWS or the isoaging mode, as described hereunder.

HWS procedure. The resin was charged in the calorimetric test cell. The test cell was fixed in the ARC furnace and the test was started with the furnace at 30°C. The electrolyte was manually added to the test cell through a syringe in one shot. The instrument works using cycles of Heat (steps of 5°C), Wait (of 15 minutes, to reach the equilibrium of the furnace) and Search of exothermic effects (the detection limit is 0.02°C/min) steps: if the instrument measures during the search period a self-heating rate of the sample equal or higher than the detection limit, it tracks the exothermic effect in adiabatic mode.

Isoaging procedure. This mode permits a sample to be held in isothermal conditions, at the set temperature for an extended time while monitoring for the start of an exothermic reaction. During the isothermal age, the sample is in adiabatic conditions. If the temperature-rise rate threshold (0.02°C/min) is exceeded, an exotherm is recognized and tracked in adiabatic mode. At the end of the isothermal age time, a standard HWS test follows. The isoaging mode tests were performed at 40°C for 48 hours. The resin and the electrolyte were charged in the calorimetric test cell. The test cell was fixed in the ARC furnace and an isothermal age test was started.

The general conditions used in all the experiments, regardless the mode used, are presented in Table 1.

Table 1. General conditions used in calorimetric tests.

Parameter	ARC
Sample amount, g, of which:	4
- resin, g	2
- electrolyte, ml	2
Test cell type	Hastelloy C
test cell weight, g	14.35
Test cell volume, ml	8
filling rate, g/ml	0.5
Φ-factor	1.65*

*using the value of 0.675 cal/g*K for the specific heat of the mixture

If the thermal inertia factor for the experiment differs significantly from that of the system, any reaction mechanism observed experimentally may not be the same as the true reaction mechanism that exists in the system being simulated. Experimental data must be corrected by the Φ-factor. The Φ-factor is estimated according to the following equation:

$$\Phi = \frac{m_{sample} \cdot c_{p,\,sample} + m_{cell} \cdot c_{p,\,cell}}{m_{sample} \cdot c_{p,\,sample}}$$

where m_{cell} is the weight of the cell and m_{sample} is the sample weight, while $c_{p,\,cell}$ is the specific heat of the cell and $c_{p,sample}$ is the specific heat of the sample. Thus, the Φ-factor is a ratio between the heat absorbed by the entire system and that absorbed by the sample alone. As the mass of the sample cell increases with respect to the cell (typical situation for a plant reactor) the Φ-factor tends to unit values. The following equations are used to correct the experimental values:

$$\Delta T_{ad} = \Phi \cdot \Delta T_{obs}$$

$$T_{fin} = T_{onset} + \Delta T_{ad}$$

$$\Delta H = c_{p,mix} \cdot \Delta T_{ad}$$

where $c_{p,mix}$ is the specific heat of the reagent mixture.

It is also possible to correct SHR data by Φ in order to obtain optimum data for the calculation of overpressure relief devices according to the DIERS methodology (for the PHI-TEC II equipment). The correction is calculated using the following mode:

$$\left(\frac{dT}{dt}\right)_{corrected} = \left(\frac{dT}{dt}\right)_{experimental}$$

The self-heat rate vs temperature plot provides information on the onset temperature of the exothermic activity and the rate of energy liberation. The temperature vs time plot provides information on the vigor of the exothermic reaction and also the available time period from the onset of exothermic activity to the end of the reaction. The pressure vs time/temperature plot provides information on the rate of pressure and temperature rise. This is useful for estimating the vent area required for the safe operation of a reactor.

Experimental

This effluent was chosen because it contains a much higher amount of palladium, copper and other metals. Silver concentration is lower in this effluent. Experiments were performed using two types of solutions: fresh industrial silver electrolyte used in electrorefining, named solution S2 and solution S2-2, obtained by acidifying solution S2 with an extra 10 % of HNO_3. By acidifying the efluent, the solution suffered a dilution of about 15%. This solution was used in order to determine the influence of the nitric acid concentration on the thermal behavior of the mixture. The composition of the fresh electrolyte used in these experiments is presented in Table 2.

Table 2. Analysis of the solution D used for calorimetric experiments

Soln	Concentration, mg/l												
	Ag	Pd	Pt	Cu	Al	Bi	Ca	Cd	Cr	Fe	Ni	Pb	Zn
S2	70000	1557	235	70000	310	-	22	300	-	30	300	212	1082

Fresh and saturated MPX-310 were evaluated. In order to saturate MPX-310, 50 ml of fresh resin were let in contact for 3 days with 1 L of silver electrolyte (S2).

The influence of fines was also studied in calorimetric test. Some resin beads where crushed and the particles under 0.250 mm were separated using standardized sieves and used in a calorimetric study as fines. Fresh resin beads with diameter higher than 0.250 mm were also evaluated.

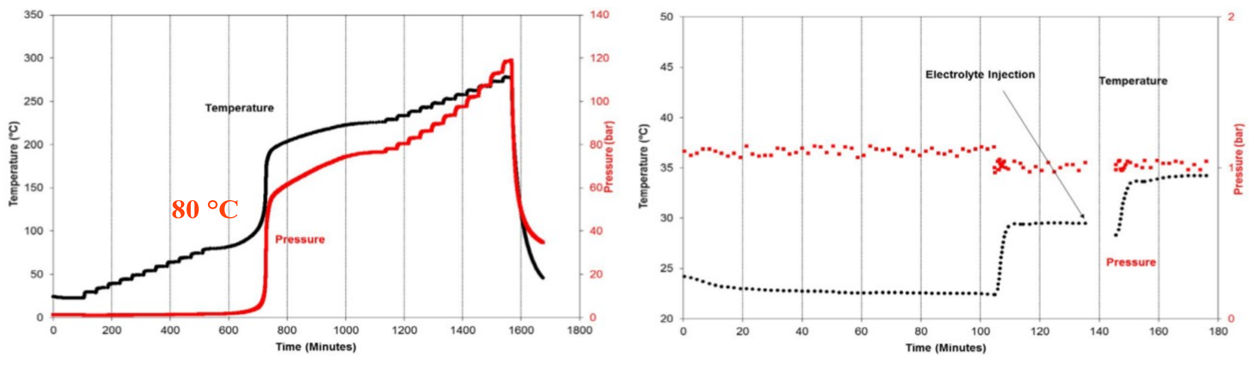
In order to verify the reactivity of the resin backbone, the support used for grafting the functionalities, SQD, was evaluated in calorimetric experiments.

1) Fresh MPX-310 resin + solution S2 (HWS mode)

For this test, fresh MPX-310 was mixed with fresh electrolyte and followed in a standard type heat-wait-search) test at 30 °C. No exothermic effect was observed when the electrolyte was injected.

The instrument detected a major exothermic effect at 80°C, tracked in adiabatic mode up to 226 °C. After this temperature, instrument continued its HWS cycles up to 277°C and then it switched in cool down mode. Between 226 and 277°C no exothermic effects were detected.

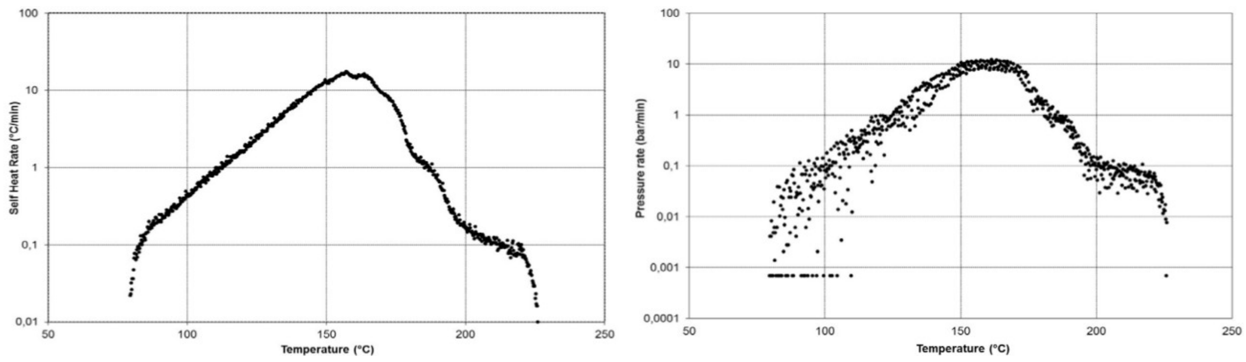
In Figure 3, the temperature and pressure towards time during the experiment are presented.



a) b)

Figure 3. Temperature and Pressure vs Time in the HWS test using fresh MPX-310 and fresh electrolyte (solution S2) from electrorefining process; a) for the whole process; b) for the first 100 minutes.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 4.



a) b)

Figure 4. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

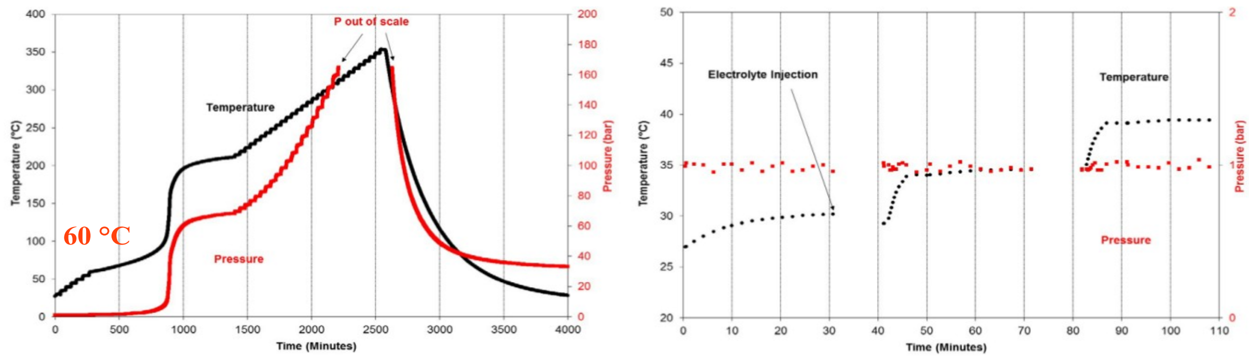
At 80 °C the TMR corrected by Φ is 107 min.

According to these first results, the onset temperature is lower for the electrorefining electrolyte, even if the copper and palladium concentrations are higher.

2) Saturated MPX-310 resin + solution S2 (HWS mode)

In this test, the behaviour of the saturated resin and fresh electrolyte mixture was studied. During the addition of the electrolyte in the test cell no temperature increase was measured. The instrument detected an exothermic effect at 60°C, tracked in adiabatic mode up to 211°C. After this temperature, instrument continued its HWS cycles up to 360°C and then it switched in cool down mode. Between 211 and 360°C no other exothermic effects were detected. Pressure was out of scale between 313°C (in heating mode) and 301°C (in cooling mode).

The temperature and pressure towards time during the experiment are presented in Figure 5.

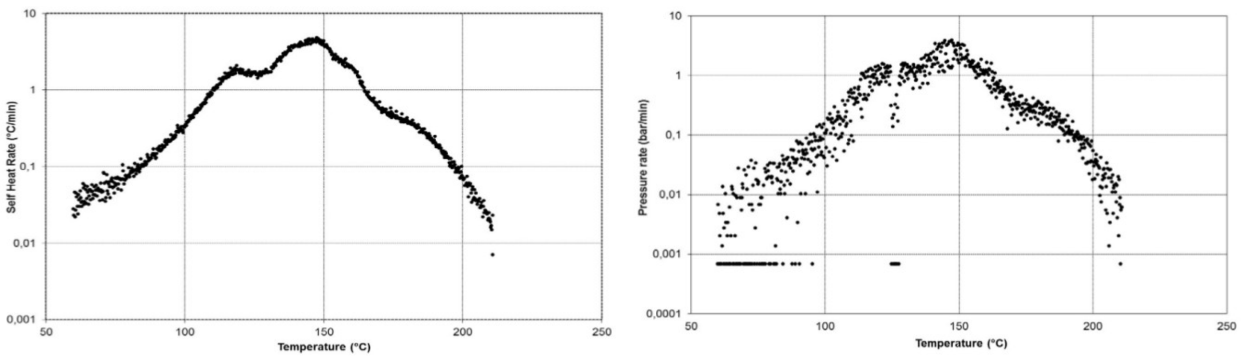


a) b)

Figure 5. Temperature and Pressure vs Time in the HWS test using saturated MPX-310 and solution S2 from electrorefining process; a) for the whole process; b) for the first 110 minutes.

In this experiment some of the pressure values were out of scale, thus a part of the parameters could not be determined accurately.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 6.



a) b)

Figure 6. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

Although in the studies using silver electrolyte from electrowinning, the saturation level on the resin didn't have a big impact on the onset temperature, in this case things are different. The onset temperature decreased with 20°C when saturated resin was used.

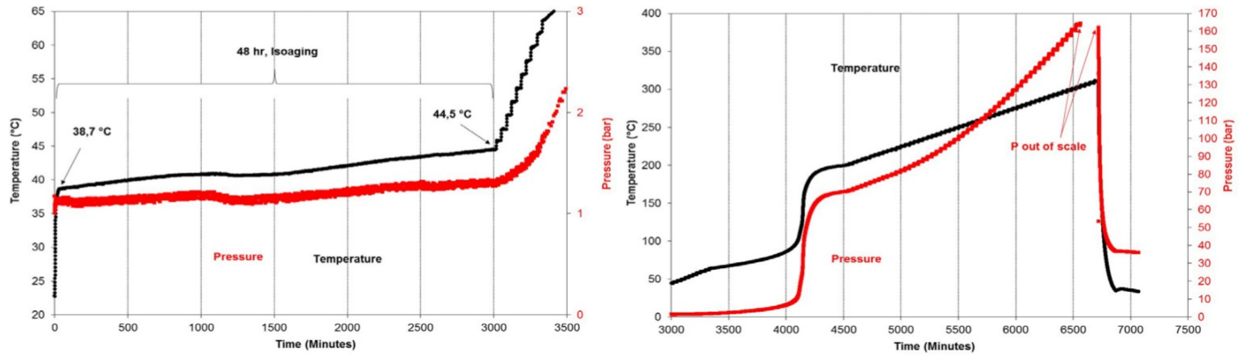
At 60 °C the TMR corrected by Φ is 355 min.

3) Saturated MPX-310 resin + solution S2 (isoaging mode)

In this experiment, the saturated resin – solution S2 mixture, previously studied in HWS mode (test 2), was studied in isoaging mode.

During the isothermal age period at 40°C, the mixture heated from 38.7°C to 44.5°C in 48 hours with a temperature rise rate lower than the threshold limit (0.02°C/min). At the end of the isothermal age period, a standard HWS test started. The instrument detected an exothermic effect at 64°C, tracked in adiabatic mode up to 199°C. After this temperature, instrument continued its HWS cycles up to 310°C and then it switched in cool down mode. Between 199 and 310 °C no other exothermic effects were detected.

The temperature and pressure towards time during the experiment are presented in Figure 7.



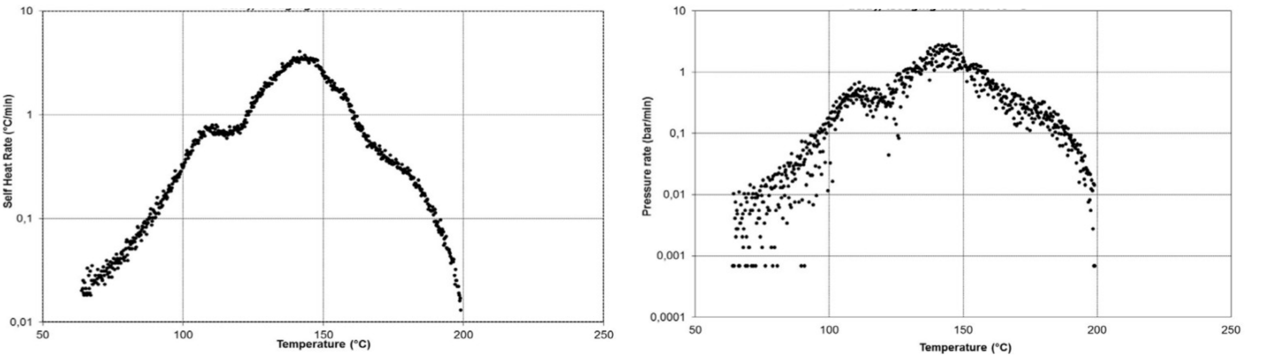
a) b)

Figure 7. Temperature and Pressure vs Time in the Isoaging test using saturated MPX-310 and fresh electrolyte from electrorefining process; a) during the Isothermal Age period; b) during the whole experiment (after the isothermal age period), including the cooling phase.

Even though the increase of temperature during the isothermal period in higher than for the electrowinning effluent, in this case the reaction doesn’t continue to runaway. The mixture has to be heat in order to initiate the runaway reaction.

The onset temperature for the HWS test following the isoaging period, is higher than in the previous test when the same mixture was evaluated directly in HWS mode.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 8.



a) b)

Figure 8. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

At 64 °C the TMR corrected by Φ is 472 min.

A comparison of the results of the HWS test on the saturated resin – solution S2 mixture (test 2) and the results of the HWS test on the same mixture but after the 48 hours isothermal age period at 40°C (test 3) is shown in Figure 9.

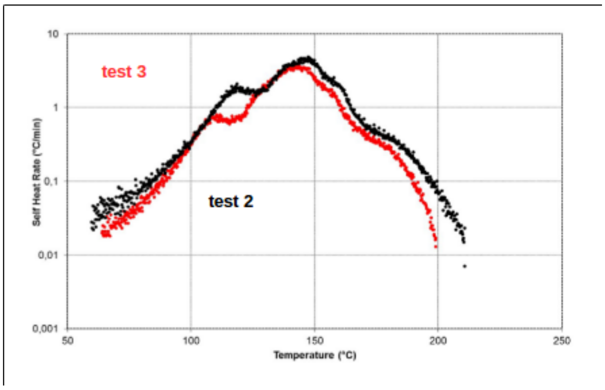


Figure 9. Comparison of the self-heating rate as a function of temperature, for test 2 and test 3.

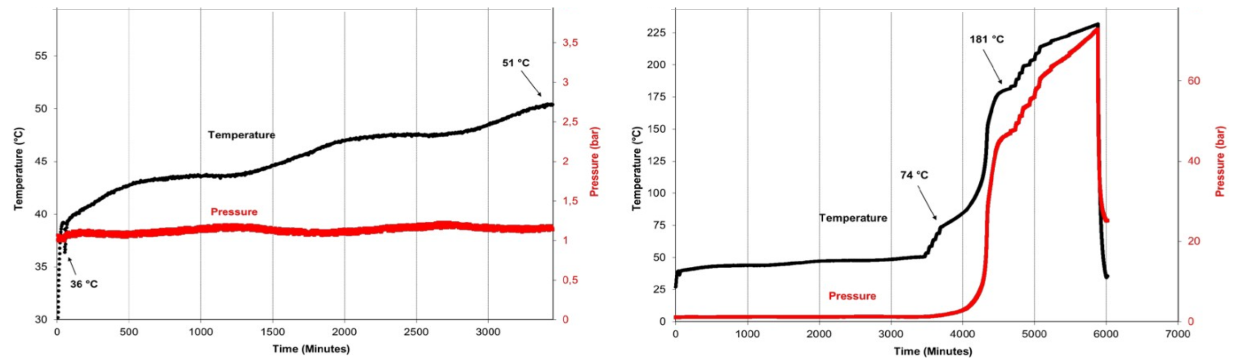
The thermal behaviour of the mixture after the isothermal age period at 40°C for 48 hours is substantially the same of the fresh mixture. It means that the thermal treating of the mixture doesn't affect its thermal behaviour.

4) Fresh MPX-310 resin, beads diameter>0.250 mm + solution S2 (isoaging mode)

In this experiment, the fresh MPX-310 resin beads with a diameter higher than 0.250 mm were mixed with solution D and studied in isoaging mode.

During the isothermal age period, the mixture heated from 36°C to 51°C in 48 hours with a temperature rise rate lower than the threshold limit (0.02°C/min). At the end of the isothermal age period, a standard HWS test started. The instrument detected an exothermic effect at 74°C, tracked in adiabatic mode up to 181°C. After this temperature, instrument continued its HWS cycles up to 230°C and then it switched in cool down mode. Minor exothermic effects (SHR near the detection limit) were detected between 200 and 230 °C.

The temperature and pressure towards time during the experiment are presented in Figure 10.

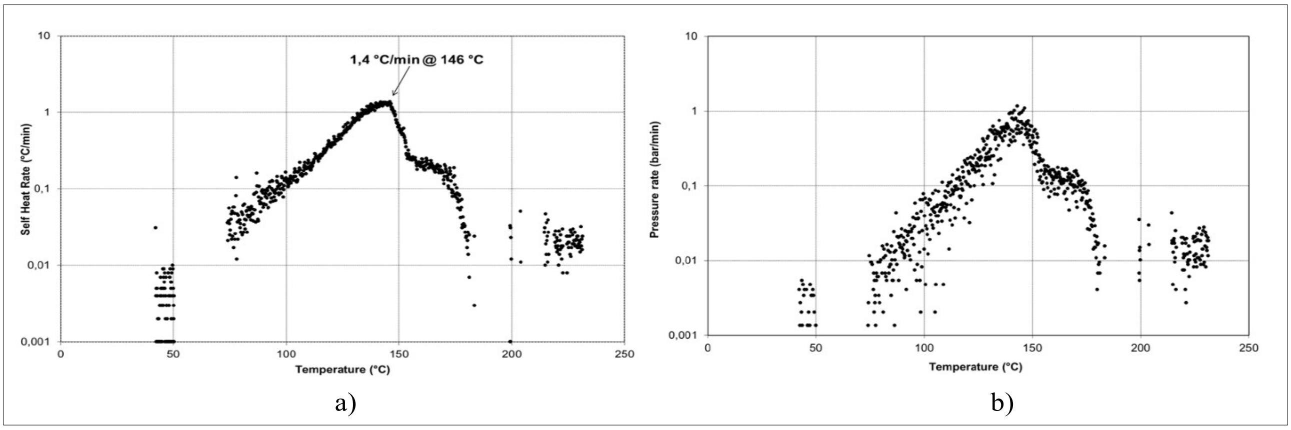


a) b)

Figure 10. Temperature and Pressure vs Time in the Isoaging test using saturated MPX-310 and fresh electrolyte from electrorefining process; a) during the Isothermal Age period; b) during the whole experiment (after the isothermal age period), including the cooling phase.

The increase in temperature during the isoaging period is higher than for the case where saturated resin is used. Despite that, the onset temperature is higher in this case, showing once again that the saturation level of the resin has an impact on this parameter.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 11.



a) b)

Figure 11. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

At 74 °C the TMR corrected by Φ is 369 min.

5) Fresh MPX-310 resin, beads diameter<0.250 mm + solution S2 (isoaging mode)

In this experiment, MPX-310 fines were mixed with solution D and studied in isoaging mode.

As soon as the electrolyte was added, the mixture started self heating from 38°C up to 42°C in 280 minutes, with the self heating rate below the threshold (0.02 °C/min); then the instrument detected an exothermic effect between 42 and 152 °C, tracked in adiabatic mode.

At the end of the exothermic effect, the instrument switched in cool down mode.

The temperature and pressure towards time during the experiment are presented in Figure 12.

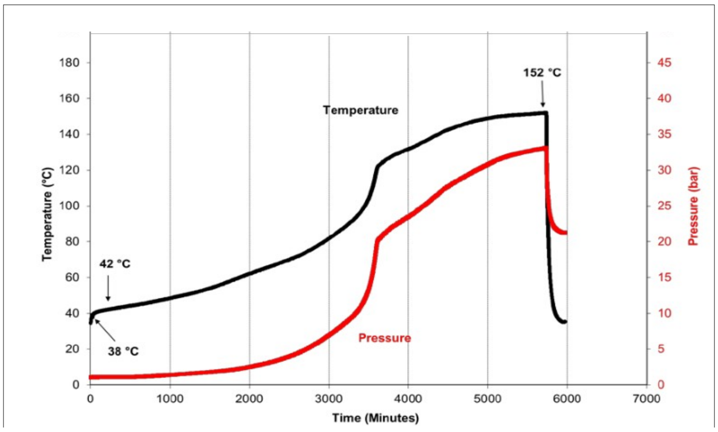
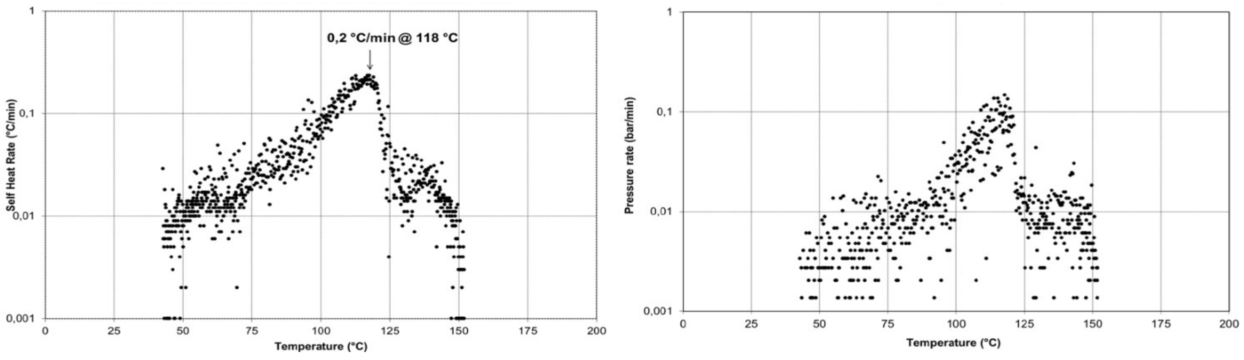


Figure 12. Temperature and Pressure vs Time in the Isoaging test using saturated MPX-310 and fresh electrolyte from electrorefining process; a) during the Isothermal Age period; b) during the whole experiment (after the isothermal age period), including the cooling phase.

For this mixture, the reaction between the resin and the electrolyte starts faster than observed in previous studies. Although the runaway takes some place after some time, the initiation doesn't need any external heating in this case. This might be related with the high specific surface of the fines.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 13.



a) b)

Figure 13. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

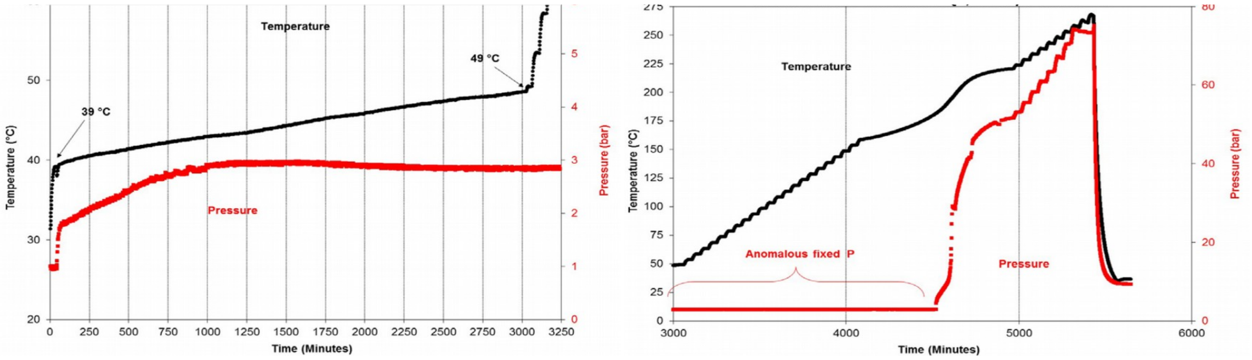
At 42°C the TMR corrected by Φ is 1921 min. The temperature at which TMR is 24 hrs, is 49°C.

6)Fresh support resin + solution S2 (isoaging mode)

The support used for preparing the MPX-310 resin was evaluated in a calorimetric test, using the isoagingg mode, followed by a HWS test. The mixture didn’t heat up when the electrolyte was added. During the 48 hours of isothermal age, a temperature rise of about 10°C (from 39 to 49°C) with a rate lower than the threshold limit (0.02 °C/min), tracked in adiabatic mode, was observed.

At the end of the isothermal age period, a standard HWS test started. The instrument detected an exothermic effect at 159°C, tracked in adiabatic mode up to 220°C. After this temperature, the instrument continued its HWS cycles up to 270°C and then it switched in cool down mode. Between 220 and 270°C no other exothermic effects were detected.

The temperature and pressure towards time during the experiment are presented in Figure 14.



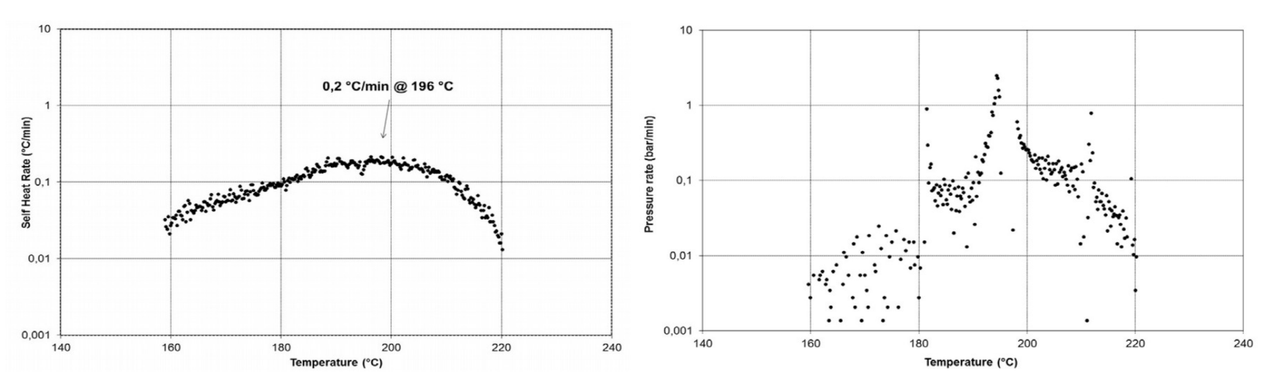
a) b)

Figure 14. Temperature and Pressure vs Time in the Isoaging test using support resin and fresh electrolyte from electrorefining process; a) during the isothermal age period; b) during the whole experiment (after the isothermal age period), including the cooling phase.

Pressure reading was anomalous (fixed) up to 180°C, probably because of a blocked tube.

The onset temperature is very high compared to the studies of MPX-310 resin.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 15.



a) b)

Figure 15. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

At 159°C the TMR corrected by Φ is 314 min.

7) Fresh support resin + solution S2-2 (isoaging mode)

In order to understand better the influence of the backbone on the MPX-310 reactivity, the support resin was also tested in a more acidic effluent.

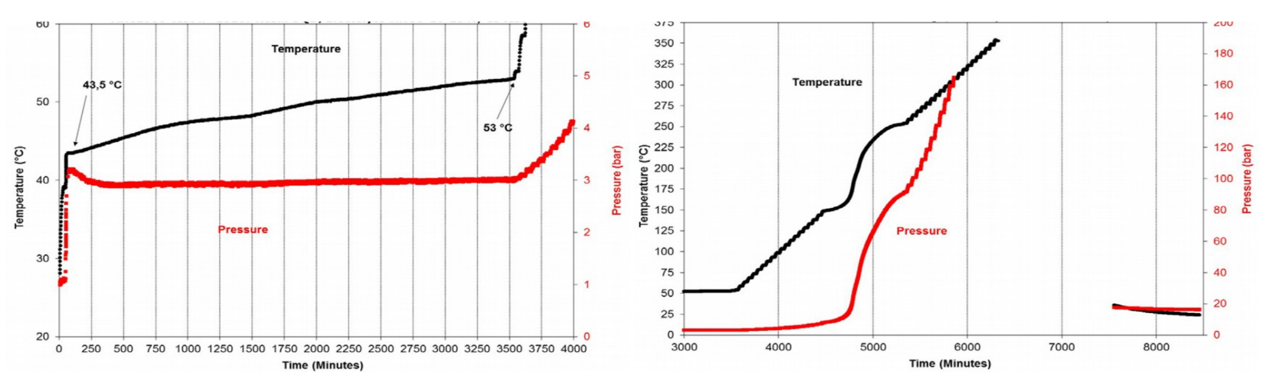
As soon as the electrolyte was added, the mixture heated from 39°C to 43.5°C. During the isothermal age period, in 48 hours there was a temperature rise from 43.5 to 53°C, with a rate near to the threshold limit (0.02°C/min), tracked in adiabatic mode.

At the end of the isothermal age period, a standard HWS test started.

The instrument detected an exothermic effect at 149°C, tracked in adiabatic mode up to 253°C. After this temperature, instrument continued its HWS cycles up to 350°C and then it switched in cool down mode. Between 253 and 350°C no other exothermic effects were detected.

Pressure was out of scale (>165 bar) starting from 307°C in heating mode. Due to a problem in the software, data were not saved during the cooling mode.

The temperature and pressure towards time during the experiment are presented in Figure 16.

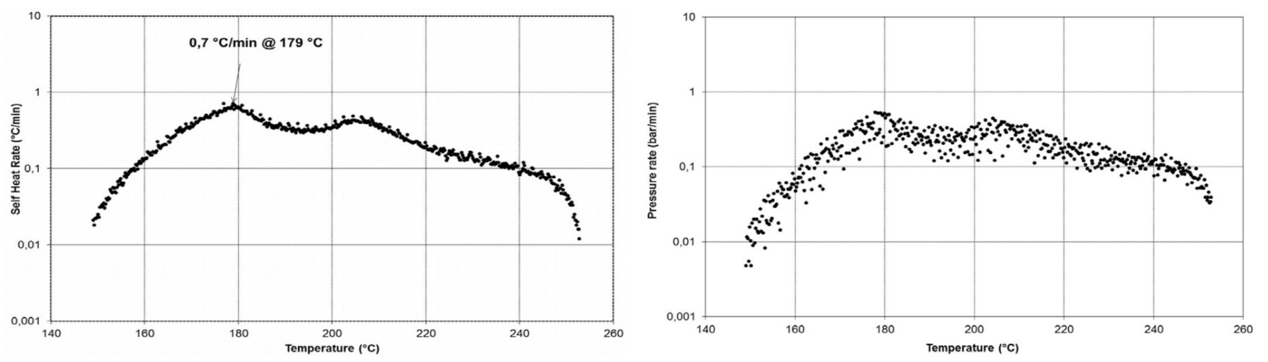


a) b)

Figure 16. Temperature and Pressure vs Time in the isoaging test using suppor resin and fresh electrolyte from electrorefining process; a) during the isothermal age period; b) during the whole experiment (after the isothermal age period), including the cooling phase.

Although the increase in temperature was higher than in the less acidic effluent, the reaction didn't self-heat to runaway. External heating was needed in oder to initiate the runaway. However, the onset temperature is much higher for the support resin than for MPX-310.

The self-heating rate and the pressure rate vs temperature during the exothermic effect tracked in adiabatic mode are presented in Figure 17.



a) b)

Figure 17. Self-heating rate (a) and pressure rate (b) towards temperature during the exothermic effect tracked in adiabatic mode

For this mixture, the pressure consists of both vapor and gas. At 149°C the TMR corrected by Φ is 168 min.

A summary of all the experiments performed using silver electrolyte used in electrorefining processes, including the main data obtained is shown in Table 3.

Table 3. Summary of the experiments performed using silver electrolyte used in electrorefining

Resin	MPX-310					Support resin	
Test	1	2	3	4	5	6	7
Resin	fresh	saturated	saturated	Fresh (>0.250 mm)	fresh (fines)	fresh	fresh
Solution	S2	S2	S2	S2	S2	S2	S2-2
Test type	HWS	HWS	isoaging	isoaging	isoaging	isoaging	isoaging
Starting temperature, T_0, °C	30	30	40	40	40	40	40
Temperature after isoaging period, °C			44.5	51	-	49	53
Onset temperature, T_{onset}, °C	80	60	64	74	42	159	149
Pressure at T_{onset}, bar	1.6	1.2	1.8	1.6	1.0	-	8.0
Max SHR, corrected by Φ, °C/min	29 at 157°C	8 at 147°C	6.8 at 142°C	2.3 at 146°C	0.4 at 118°C	0.3	1.15

Max pressure rate, bar/min	12 at 157°C	4 at 147°C	2.9 at 145°C			-	0.52 at 179°C
Final temperature, T_{fin}, °C	226	211	199	181	152	220	253
Pressure at T_{fin}	77	68	70	46.8	33	52	90
ΔT_{ad} corrected by Φ, °C	244	251	224	181	188	100	172
Enthalpy, calculated with $c_{p,mixture}$ = 2.8 J/g°C, kJ/kg mix	-688	-710	-627	-510	-530	-280	-480
Φ-corrected TMR, minutes	107 at 80°C	355 at 60°C	472 at 64°C	369 at 74°C	1921 at 42°C	314 at 159°C	168 at 149°C

In normal conditions, the onset temperature for the MPX-310 and this type of effluent is 80°C (1). When saturated resin is used, the runaway reaction is initiated at a lower temperature, 60°C (2). The maximum SHR and the maximum pressure rate are much higher when fresh resin is used (1).

When the saturated resin is used in a isoaging test (3), the temperature increases with almost 5°C during the isothermal period. The thermal behaviour of the resin is changed after the isoaging periods, and the onset temperature is higher than in the HWS test for the same mixture.

The fresh resin – fresh electrolyte mixture heats up with 11°C during the isothermal age time (4). However, the onset temperature is 74°C, higher than for the saturated resin, showing that the saturation level on the resin contributes to the initiation of the runaway reaction.

Fines have a major effect on the onset temperature. The reaction self-heats up to runaway if no heat transfer with the external environment is provided (5).

The point of the major exotherm of the non-functionalised support was much higher than the major exotherm of MPX-310 under similar conditions, indicating that the functionality that is grafted on the support is the more likely cause of the major exotherm than the nature of the support (6 and 7).

Although the mechanism of the reaction was not understood and cannot be deduced, the calorimetry studies help on setting some boundary condition were the process can be run safely. Fines can influence the initiation of the runaway reaction (test 5) and they should be removed before starting the filtration process. The resin should not be allowed to stay in contact with fresh electrolyte when the installation is stopped; the effluent should be evacuated and replaced with water.