DE LA RECHERCHE À L'INDUSTRIE

LANTHANIDES CHLORIDES ELECTROWINNING

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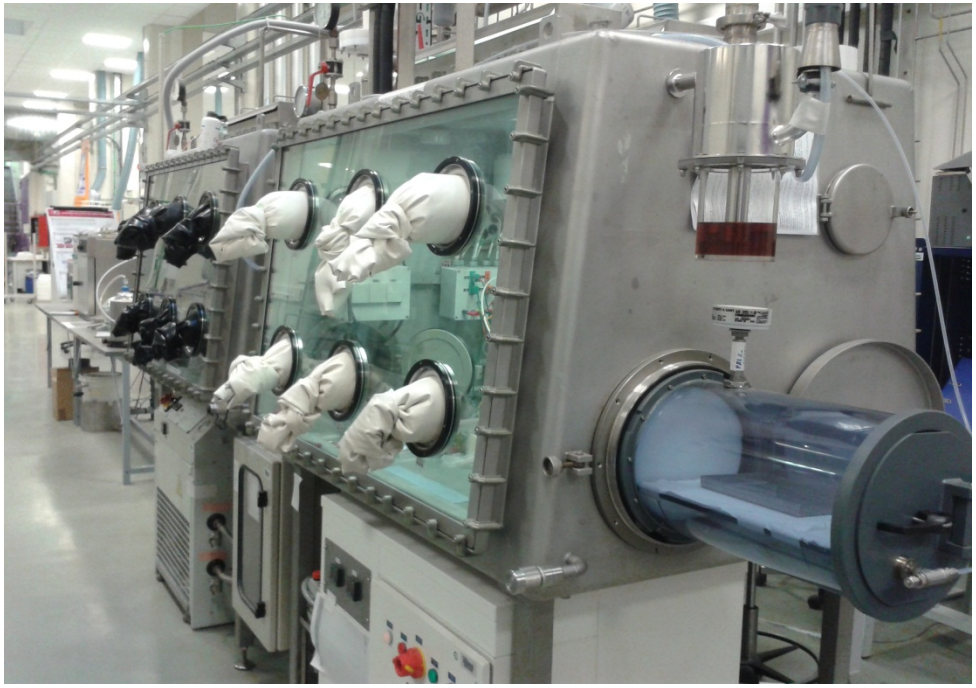
LANTHANIDES CHLORIDES ELECTROWINNING

- Electrorefining salt cleaning
- Aluminium and solid inert cathodes
- Cl_2 impact on deposition efficiency

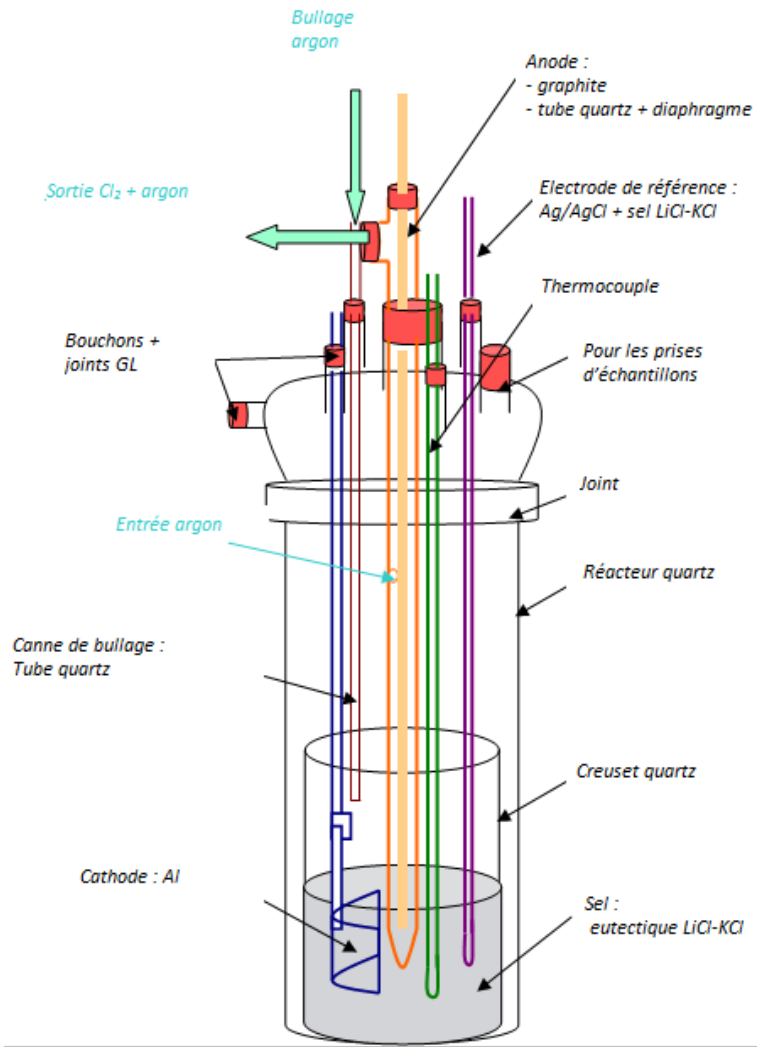


Ar glove-box, < 10 ppm H_2O and O_2

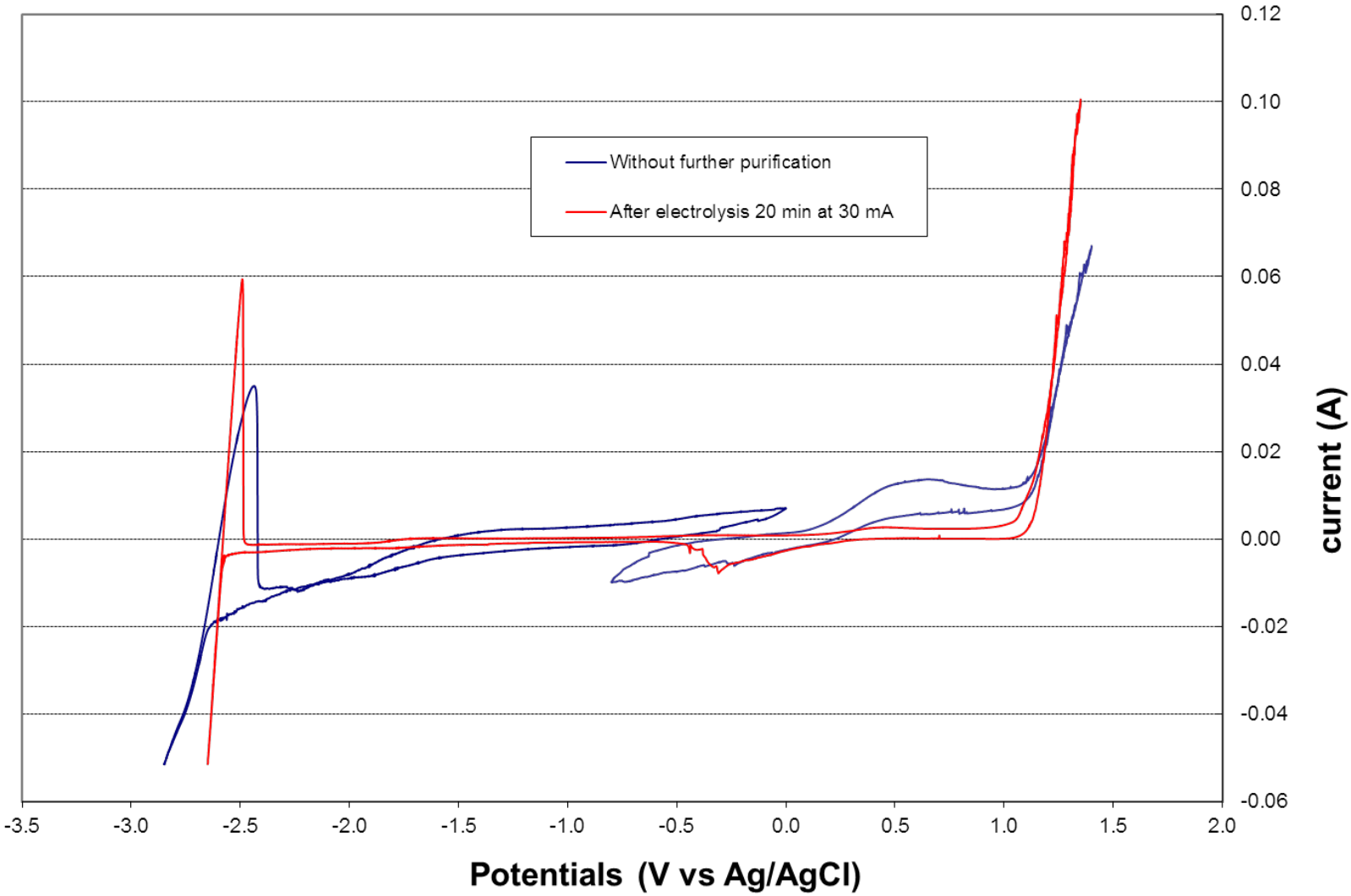
Quartz cell

EXPERIMENTAL CONDITIONS

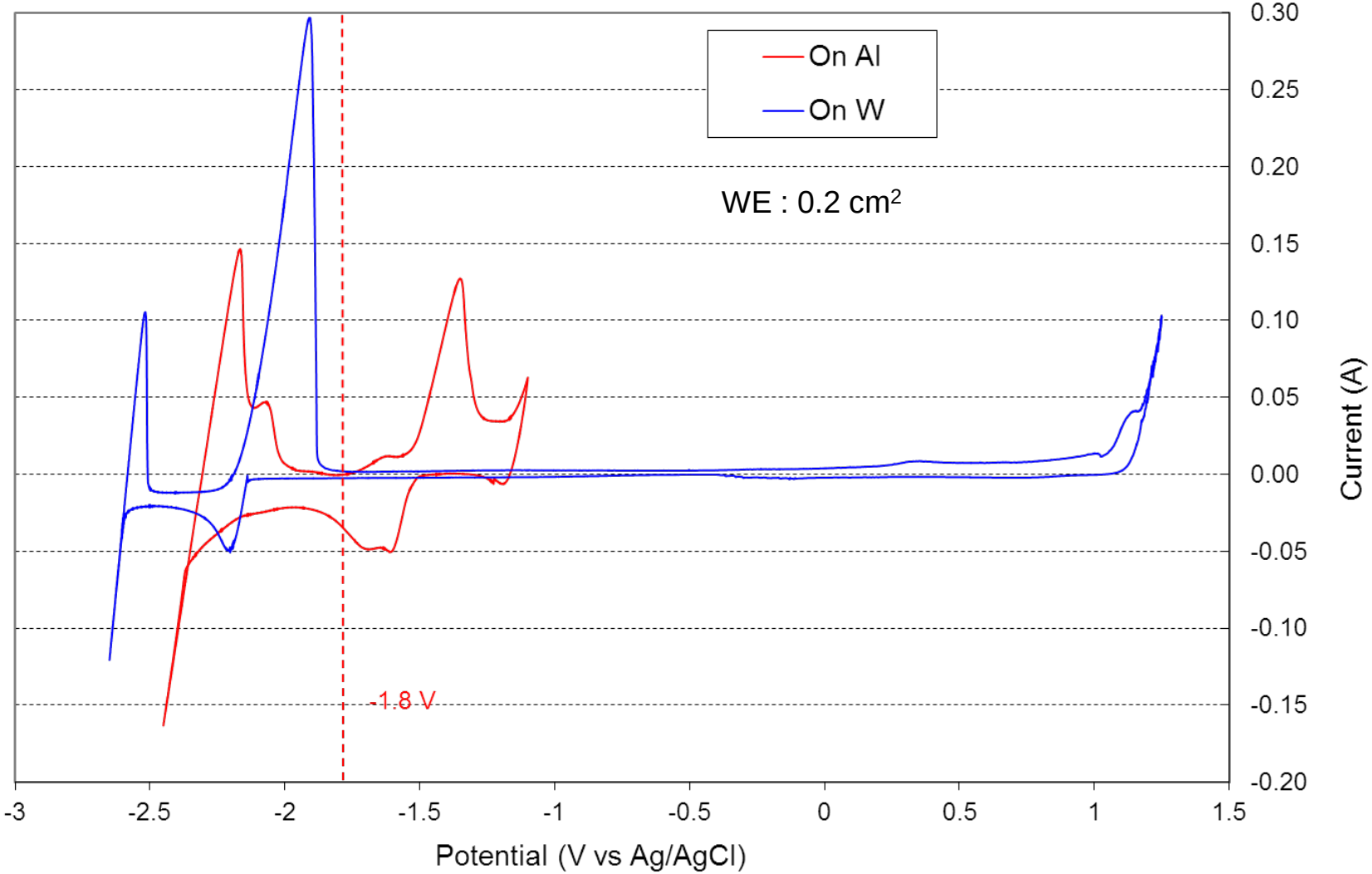
- LiCl-KCl stored at 190°C under vacuum
- 50 g of LiCl-KCl eutectic per experiment
- Alumina crucible
- Oven temperature : 450°C
- Initial [Ce^{3+}] : mainly 0.5wt%, $CeCl_3$ 99,99%, addition is done the day before (slow dissolution rate)
- Constant current electrolysis
- Cut-off potential : -1.8 V
- Argon flow : 4-8 L/h
- Aluminum cathode surface : 12 cm²



SALT PURIFICATION BEFORE $CeCl_3$ ADDITION

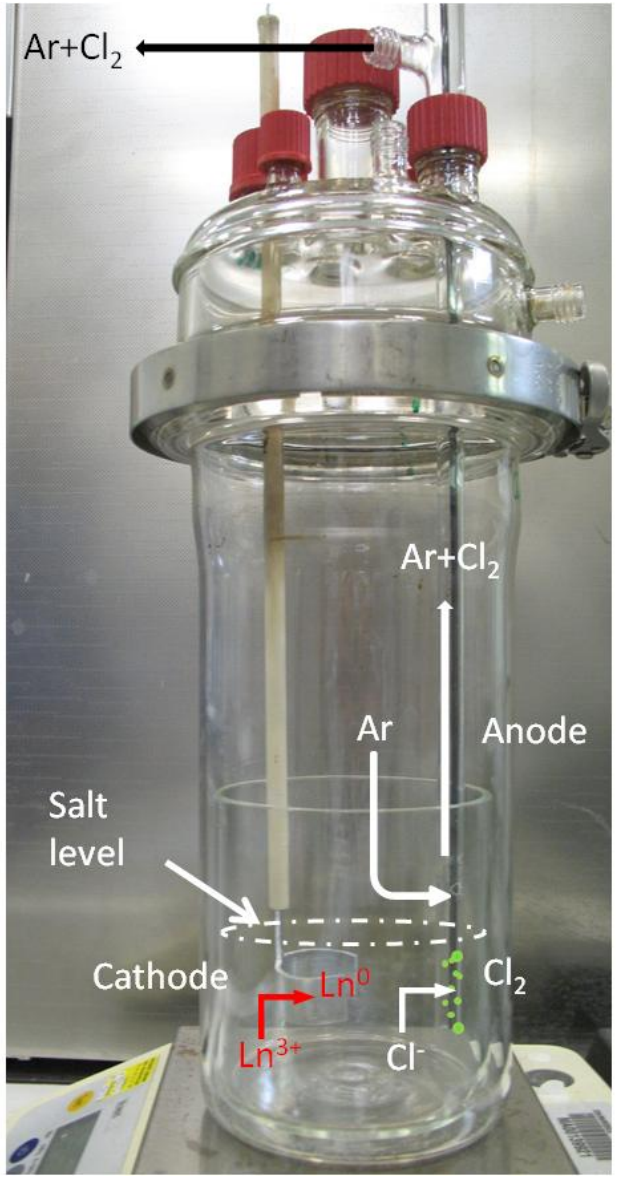


VOLTAMMETRY



EXPERIMENTAL CONDITIONS

Quartz anode with and without diaphragm (0.5 mm hole)



CHEMICAL ANALYSIS

- Salt sampling (~100 mg)
- Dissolution in 10 mL HNO_3 (1M).
- Electrodes : dissolution in HNO_3 (7M), heated overnight (~50°C)
- ICP-AES analysis

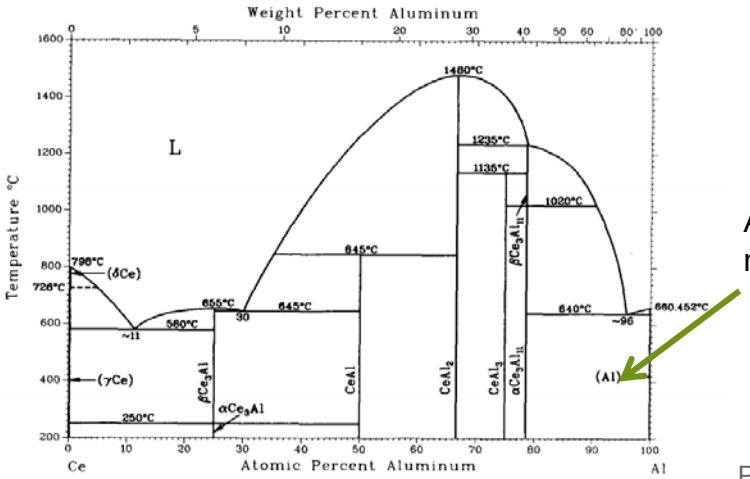
$m_{Al\ initial}$ (g)	$m_{Al\ final}$ (g)	m after HNO_3 (g)	Δm after HNO_3	n Al dissolved (mol)	n Ce (mol)	n Al/n Ce
8.4513	9.7005	8.1438	0.3075	1.14E-02	3.41E-03	3.3
6.969	7.6126	6.8341	0.1349	5.00E-03	1.43E-03	3.5
7.3545	8.0508	7.2342	0.1203	4.46E-03	1.23E-03	3.6
6.8781	8.0665	6.5929	0.2852	1.06E-02	3.41E-03	3.1

$$m_{theo} = \frac{M_{Ce}}{3F} I \times t$$

$$Rf = \frac{m_{ICP-AES}}{m_{theo}}$$

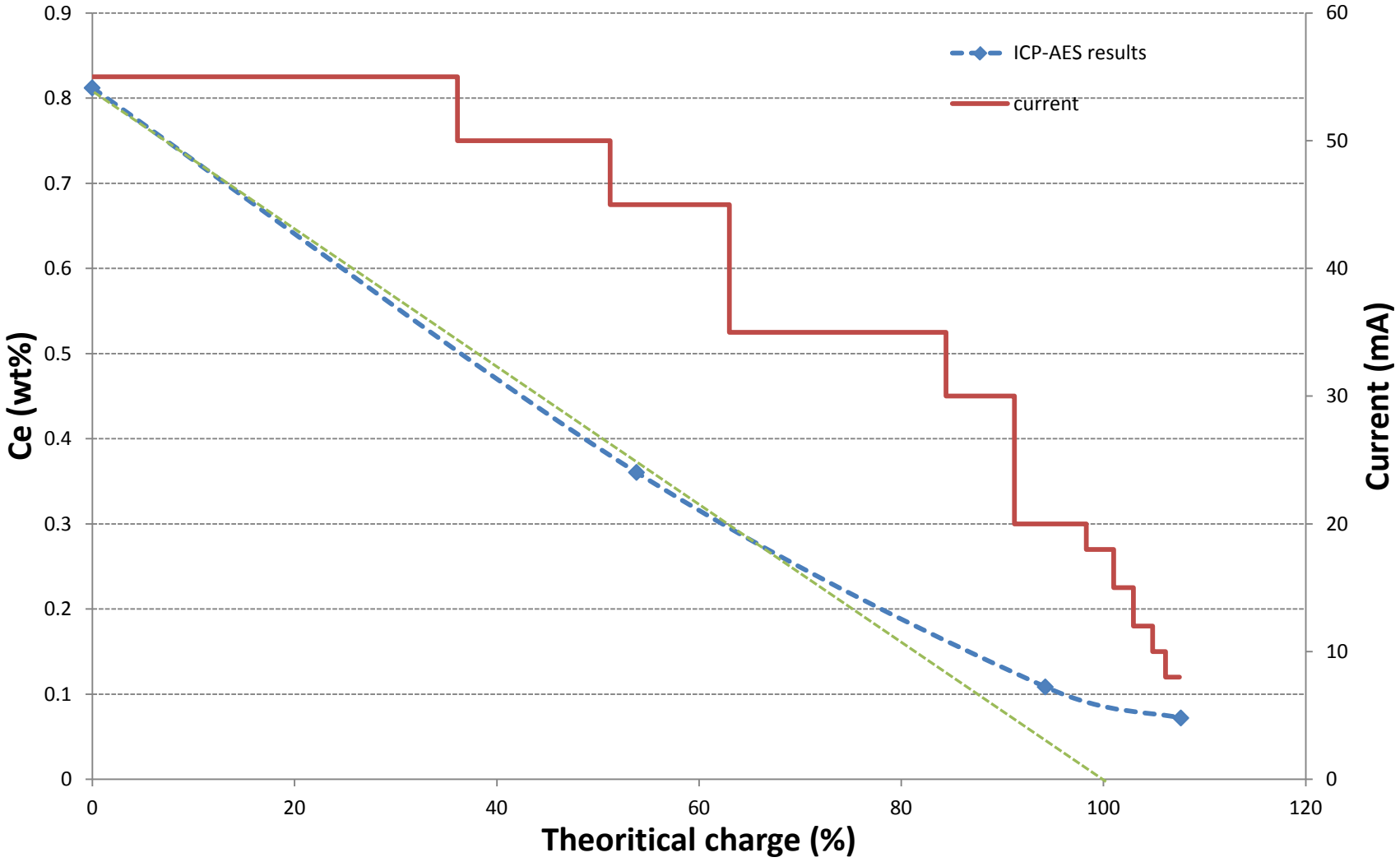
$$R = \frac{masse_{deposit}}{masse_{removed}} = \frac{m_{ICP-AES}}{(m_{Ce_{initial}} - m_{Ce_{final}})_{salt}}$$

$$\tau = 1 - \frac{m_{Ce_{final}}}{m_{Ce_{initial}}}$$

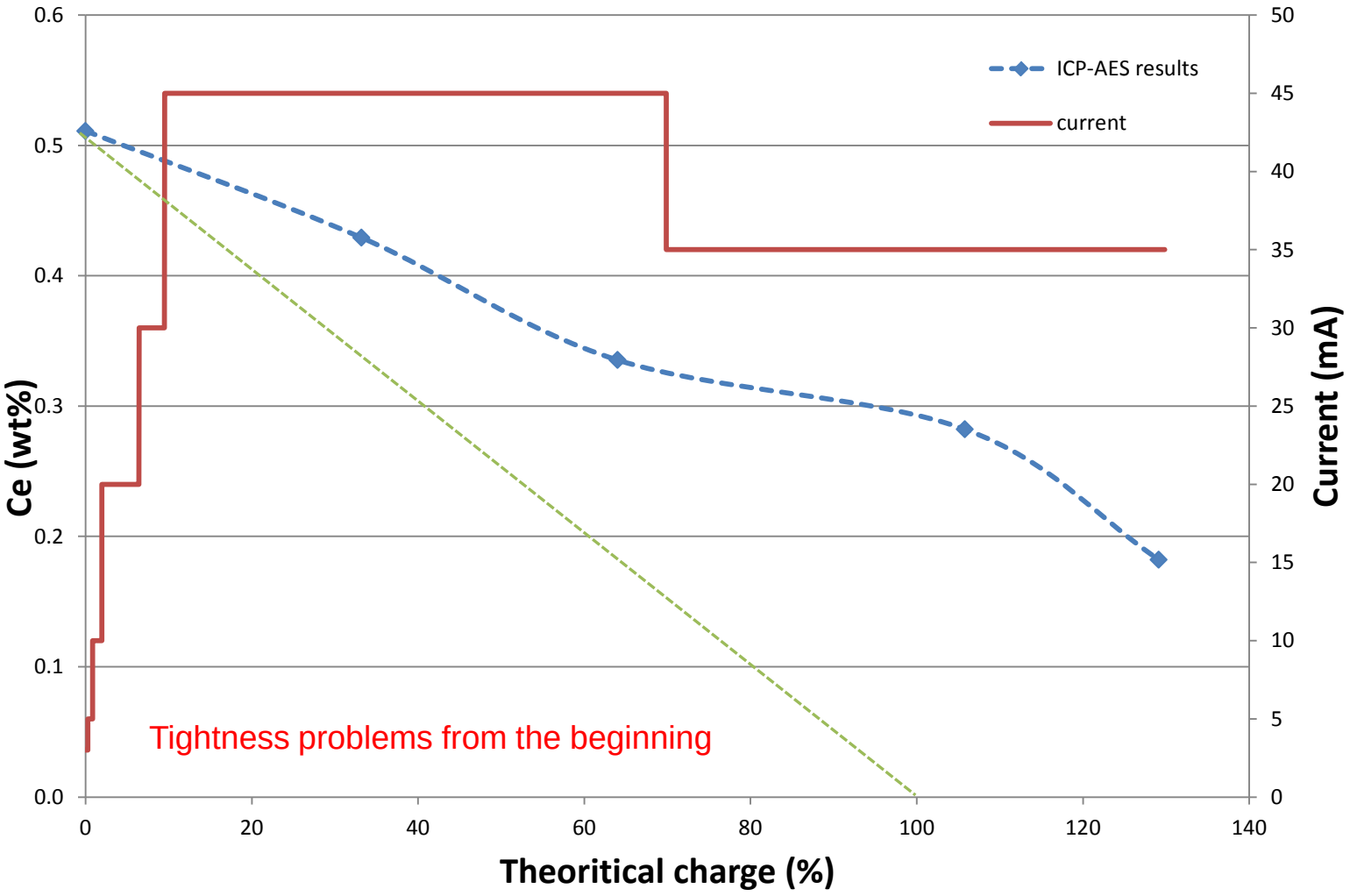


$Al_{11}Ce_3$
nAl/nCe ~3.7

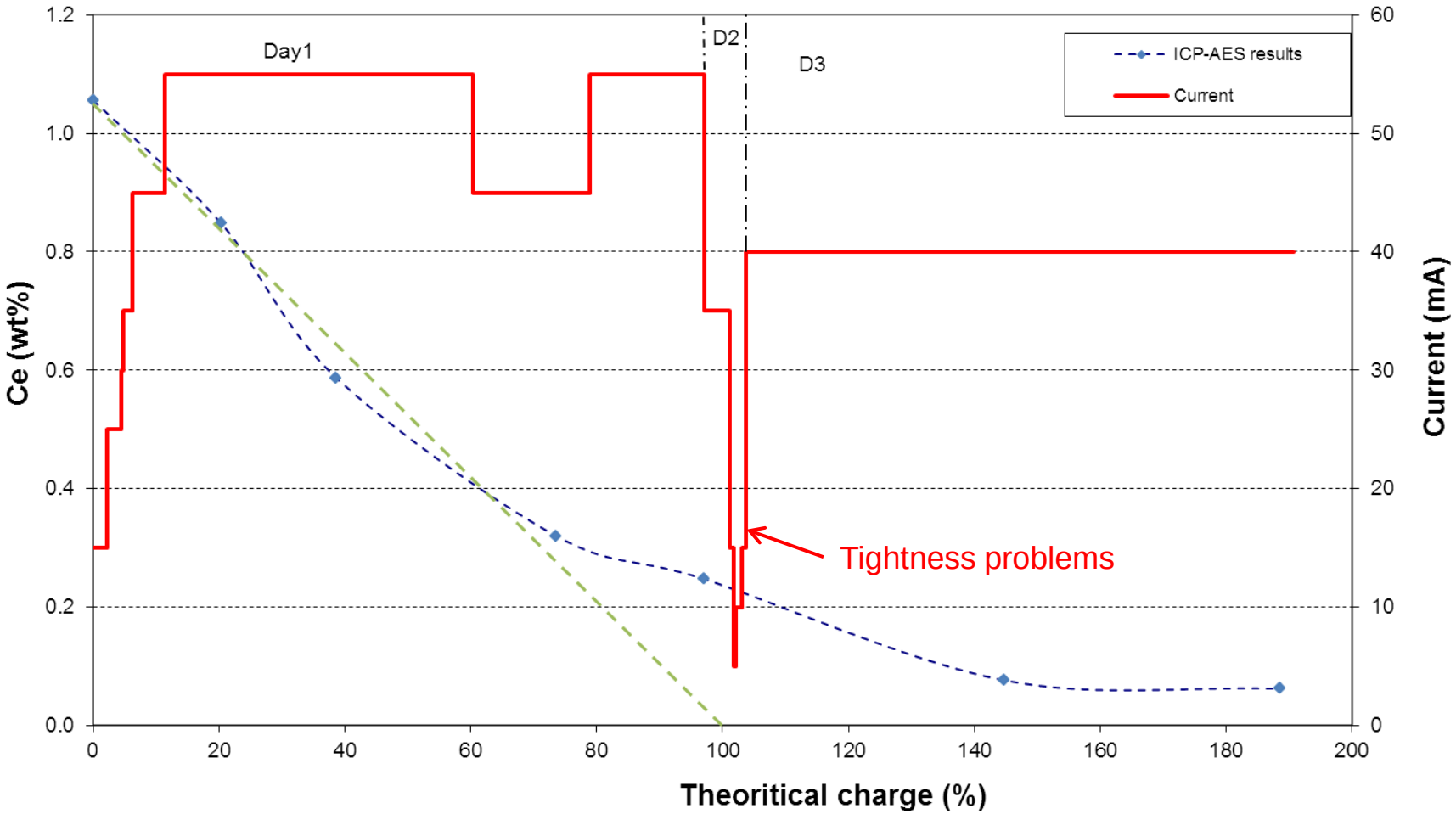
CONCENTRATION PROFILE – RUN 4 (WITH DIAPH)



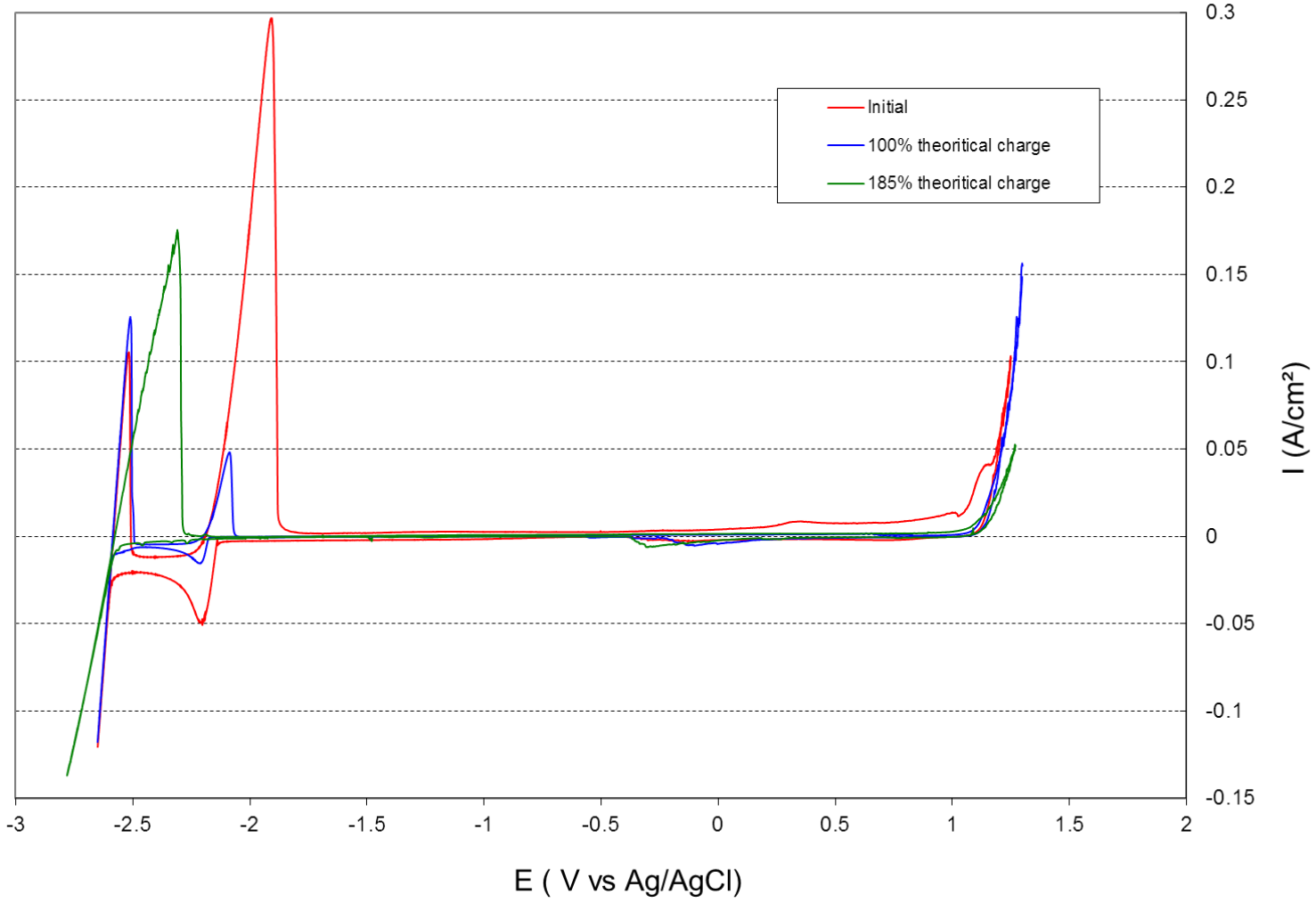
CONCENTRATION PROFILE – RUN 2



CONCENTRATION PROFILE – RUN 1 (WITHOUT DIAPH)



VOLTAMMETRY – RUN 1



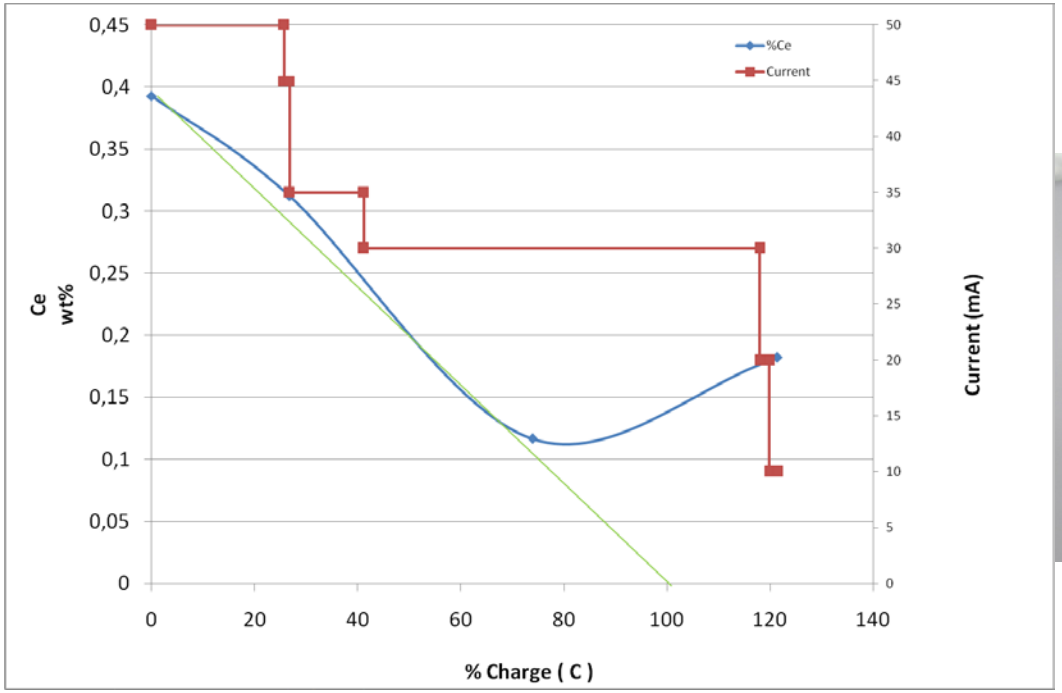
EXPERIMENTAL RESULTS

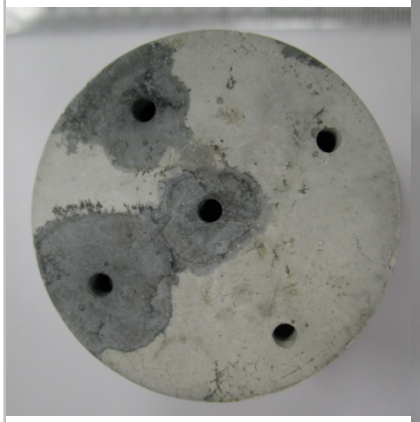
Anode		[Ce] (wt%)	[Ce] (mg)	[Ce] f (wt%)	[Ce]f (mg)	Q cleaning	Q (C)	Q (%)	m_{theo} deposit (mg)	m_{icp} (mg)	Rf (%)	R (%)	τ (%)
Glassy carbon without diaphragm	1	0,519	267	0,182	92	543	697	130	337,1	181	54	103	66
	2	1,056	536	0,062	30	1109	1967	177	951,2	478	50	94	94
	3	0,489	247	0,101	50	511	529	104	255,8	200	78	102	80
Glassy carbon with diaphragm	4	0,985	499	0,04	24	843	908	108	439,1	478	109	101	95
Graphite without diaphragm	5	0,57	293	0,1	50	605	586	97	283,4	308	109	127	83
	6	0,43	214	0,03	16	442	606	137	293,1	199	68	101	93
Graphite with diaphragm	7	0,45	224	0,06	28	463	434	94	209,9	225	107	115	88
	8	0,519	259	0,05	25	536	677	126	327,4	240	73	103	90
Anode		[Nd] (wt%)	[Nd] (mg)	[Nd] f (wt%)	[Nd]f (mg)	Q cleaning	Q (C)	Q (%)	m_{theo} deposit (mg)	m_{icp} (mg)	Rf (%)	R (%)	τ(%)
Glassy carbon without diaphragm	9	0,446	226	0,03	18	466	731	156	353,5	225	64	108	92
Glassy carbon with diaphragm	10	0,455	230	0,07	32	463	662,5	143	320,4	211,6	66	107	86

ELECTROWINNING ONTO INERT ELECTRODES

- Mass balance evaluation is more difficult
- Deposit adherence
- Set-up under development (boron nitride and alumina cathode container are tested)

Q (C)	$m_{Ce\ Theo}$ (g)	$m_{Ce\ electrode}$ (g)	$m_{Ce\ container}$ (g)	Recovery (%)
2957,5	1,431	0,772	0,286	74

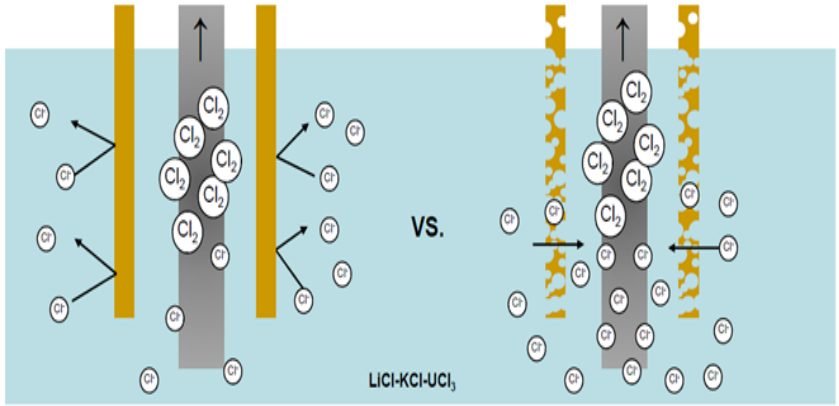




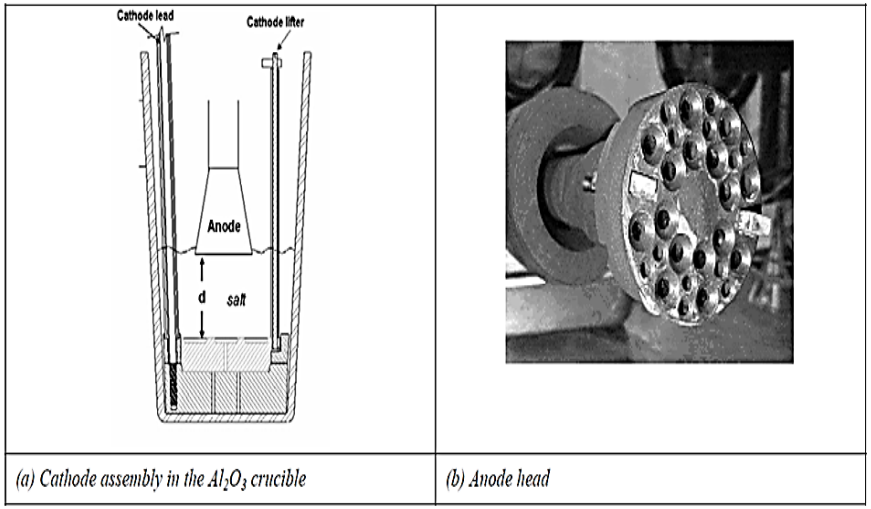
SUMMARY

- 95% of the metal can be recovered onto Al electrode
- 0.05 wt% < final concentration < 0.1wt%
- Good mass balance between the amount of metal removed from the solution and the metal found on the electrode
- The Ar flow that facilitates the Cl_2 extraction sounds to be a key parameter for the current efficiency
- No real difference between glassy carbon and graphite
- Diaphragm improves the recovery yield and decrease the electrolysis length but is not easy to work with (as it is conceived now)
- U, Pu, Am recovery tests will be carried out soon

KAERI's set-up



ANL's set-up



(a) Cathode assembly in the Al_2O_3 crucible | *(b) Anode head*