ON THE CHEMICAL NATURE OF THE BIOCIDE IN THE FLIGHT WATER AND ITS INTERACTION WITH THE STAINLESS STEEL SURFACE

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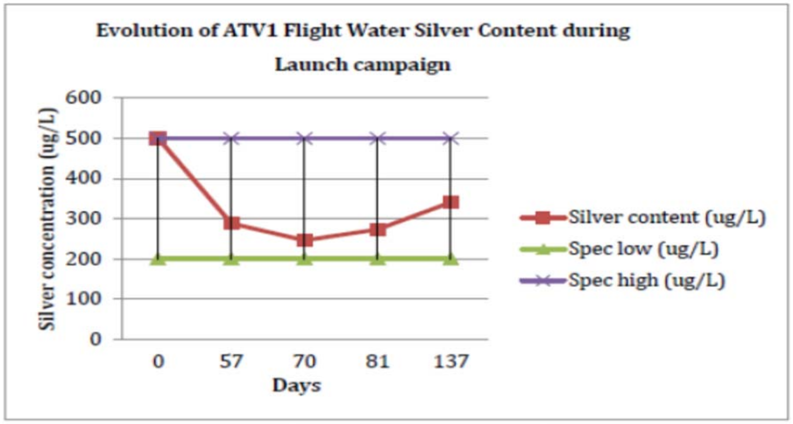
ACTINIUM CHEMICAL RESEARCH

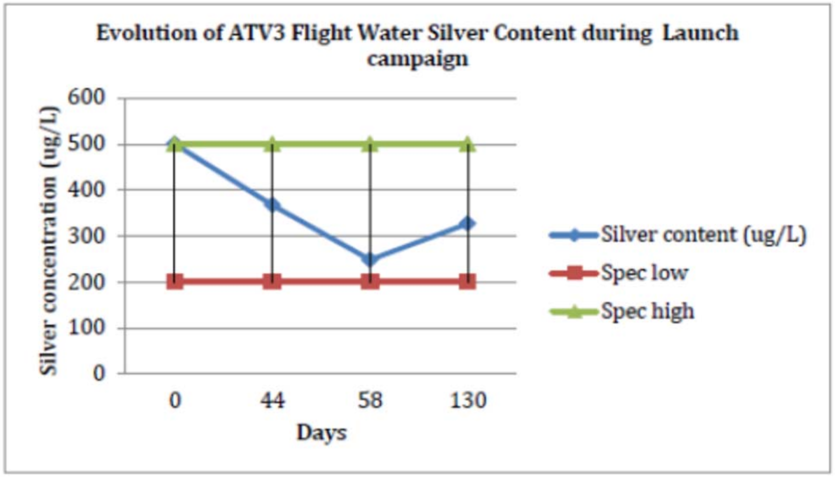
Silver as biocide in potable water

- Potable water for the astronauts of the International Space Station (ISS) is produced by SMAT in Turin (Italy)
- The potable water is silverized (silver addition) to prevent the bacterial and algae growth during water storage.
- The silverized water once prepared in Turin is transferred to Kouru (French Guinea) ready to be lauched to the ISS.
- Reaching the ISS, the silverized water is stored in special tanks there.

Problem: variation of the silver content in the potable water destined to ISS



Evolution of ATV1 Flight Water Silver Content during Launch campaign



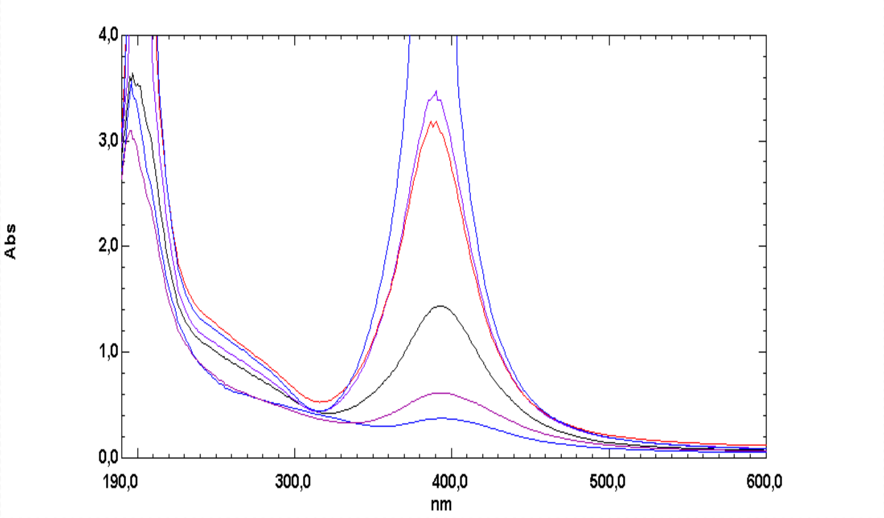
Evolution of ATV3 Flight Water Silver Content during Launch campaign

- The graphs in the left show the variation of the silver concentration in the potable water (or LBC) destined to ISS.
- The surfaces of the tanks where the LBC is in contact are stainless steel AISI 316L or a perfluoroplastic known as Teflon-FEP

Electrochemical silverization

- In the preparation of the flight water for ISS, the first stage consists in the addition of NaF to spring water followed by electrolysis.
- At this stage there is the formation of insoluble AgCl particles due to the presence of chlorides in the ground water. It is necessary to proceed with a microfiltration to remove AgCl particles which are in colloidal liophobic state.
- The filtration is made through 0.45 micron filter.
- Then the electrolysis between silver electrodes is repeated again until the desired total Ag^+ concentration of 10 mg/L (HBC) or 0.5 mg/L (LBC) is reached and then the water is micro-filtered again through the 0.45 micron filter before storage and transportation.

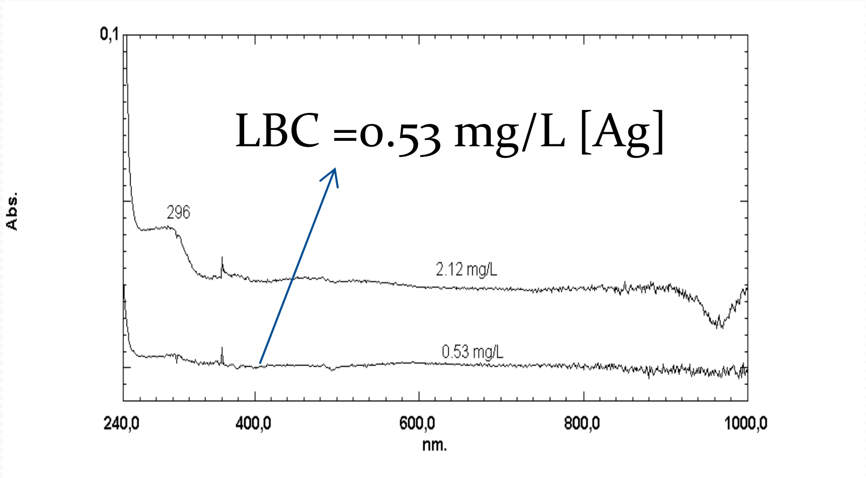
Features of metallic silver nanoparticles in colloidal dispersion

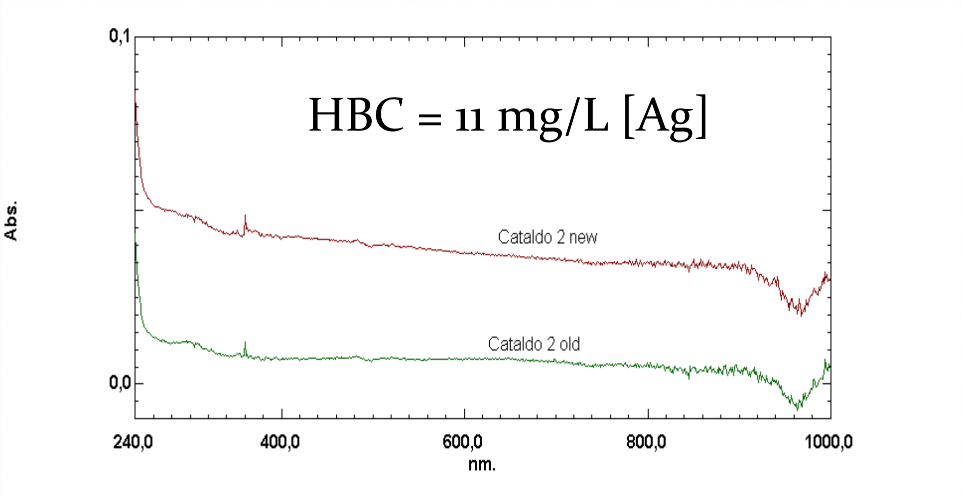


- Ag° colloidal solutions display an electronic spectrum at about 400 nm due to surface plasmon resonance
  (collective oscillation of the free conduction electrons induced by an interacting electromagnetic field form incident photon radiation)

- Tyndall effect which consists in the light scattering caused by the dispersed metal nanoparticles

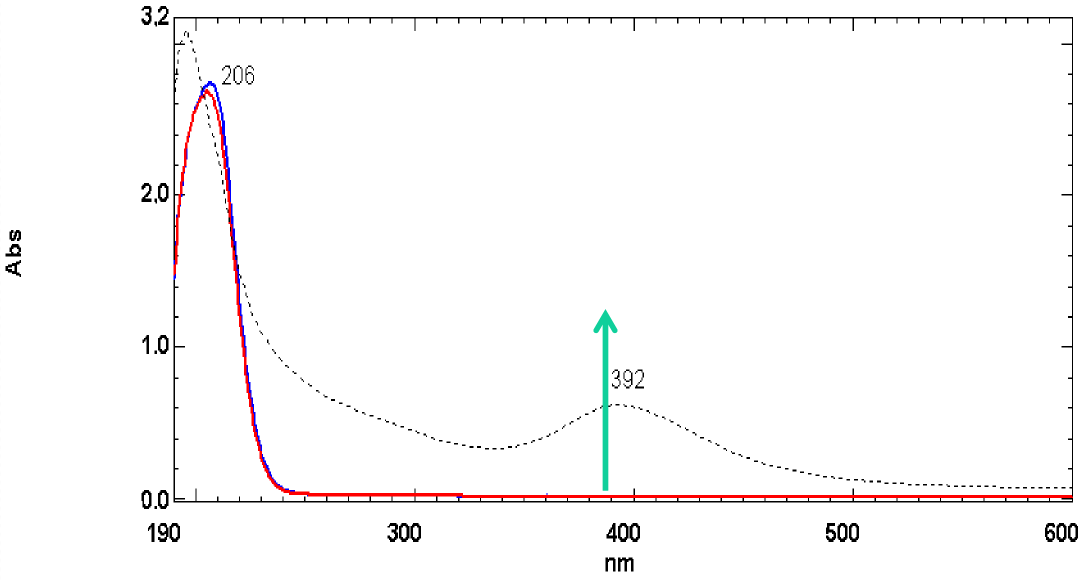
The silverized water for ISS does not show the surface plasmon resonance band


LBC =0.53 mg/L [Ag]


HBC = 11 mg/L [Ag]

- No surface plasmon resonance band is shown neither by LBC nor by HBC.
- **Thus, no metallic colloidal silver is present in the potable water but only ionic-colloidal silver**

Addition of a reducing agent to LBC or HBC produces the SPR band



Electronic absorption spectra of pristine LBC and HBC water samples. Both samples show only an absorption peak in the deep UV, at 206 nm (blue and red lines) confirming the ionic colloidal nature of the solute.

On the other hand, the dotted line due to metal silver nanoparticles generated by the addition of $NaBH_4$ to $AgNO_3$ solution shows a peak at 392 nm due to the SPR band of silver particles.

Ionic-colloidal silver in Ag^+ form

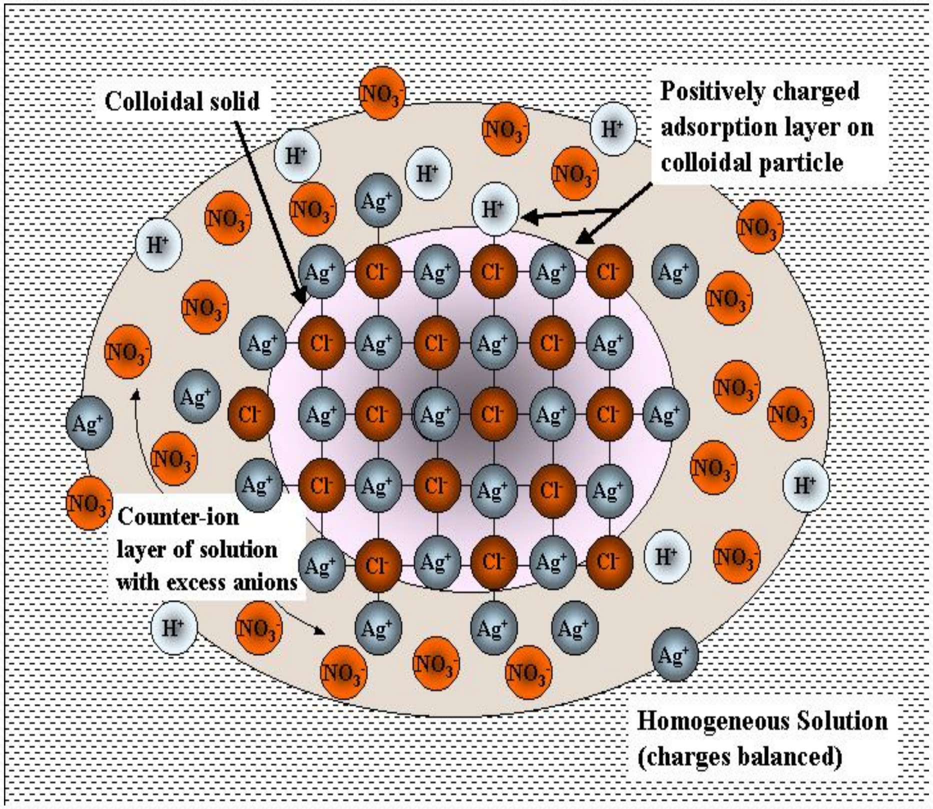
- Colloidal particles of **insoluble silver salts** behave as liophobic colloids which are kept as sols by the interaction with other ions present in solution. Thus, AgCl may interact with the excess of Ag^+ ions (but also Ca^{2+} and Mg^{2+} for example) to give:

$[(AgCl)Ag^+]X^-$
$[(AgCl)_2Ca^{2+}]2X^-$
$[(AgCl)_2Mg^{2+}]2X^-$
and
$[(AgCl)X^-]Ag^+$
$[(AgCl)X^-]_2Ca^{2+}$
$[(AgCl)X^-]_2Mg^{2+}$

In these conditions there is no trace of metallic silver nanoparticles.

Silver halide colloidal particles do not absorb in the visible but show an absorption band at 270-280 nm in the UV, consequently are easily distinguishable from metallic silver nanoparticles

Model of Ionic-Colloidal silver in Ag^+ form



A model of colloidal silver salt nanoparticle in colloidal state.

- The microparticle of the insoluble silver salt is surrounded by adsorbed ions and at higher distance by loosely bound couterions

- The electrical double layer which is measured as Z-potential arises from the surface of adsorbed ions on the colloidal particle and the loosely bound counter-ions.

Interaction of LBC with SS AISI 316L or Teflon-FEP surfaces

- The silver load of LBC was followed in laboratory using purposely built stainless steel tanks with different surface treatments i.e. electropolishes or acid passivated.

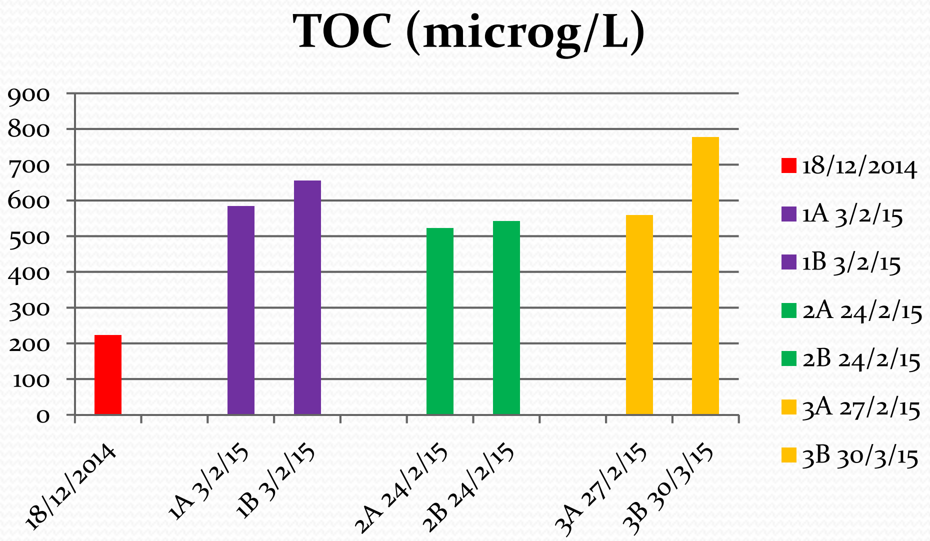
- The silver load of LBC was followed in laboratory using teflon-FEP tanks.

Summary of activities on SS tanks

- Tanks 1A, 2A and 3A → Electropolished
- Tanks 1B, 2B → Acid passivated
- Tanks 1A, 1B filled with LBC and cut and surface analyzed when Ag^+ → zero
- Tanks 2A, 2B filled again after LBC Ag^+ → zero. The new re-filling with 2.6 mg/L Ag and monitored to build a kinetics curve
- Tank 3A filled with LBC under N2, LBC Ag^+ → zero.

ALL DATA IN MICROGRAMS / L			SMAT	**Acti-nium**	**Acti-nium**	**CNR-IMC**	SMAT	**Acti-nium**	**CNR-IMC**	SMAT	**Acti-nium**	**CNR-IMC**	SMAT	**Acti-nium**	**CNR-IMC**	SMAT	**Acti-nium**	**CNR-IMC**	SMAT	**Acti-nium**	SMAT	**CNR-IMC**
			ICP-MS	Photometric	Photometric	ICP-MS	ICP-MS	Photometric	ICP-MS	ICP-MS	Photometric	ICP-MS	ICP-MS	Photometric	ICP-MS	ICP-MS	Photometric	ICP-MS	ICP-MS	Photometric	ICP-MS	ICP-MS
	Specification	**Typical values**	at filling	at filling	at filling	BLANK	1A	1A	1A	1B	1B	1B	2A	2A	2A	2B	2B	2B	3A	3A	3A	3A
			18/12/2014	09/01/2015	03/02/2015	<------	------>	03/02/2015	<------	------>	03/02/2015	<------	------>	24/02/2015	<------	------>	24/02/2015	<------	------>	27/02/2015	30/03/2015	<------
TOC	**<20000**	**500**	**223**				**585**			**656**			**522**			**542**			**560**		**777**	
B			<20			23,5	<20		35,7	<20		15,9	<20		16,8	<20		15,7	<20			15,8
Na			7000																			
Mg	3000-50000	13000	17700																			
Al			<5		5	2,3	<5	14	3,4	<5	13	1,9	<5	7	2,3	<5	8	1,6	<5	4		2,1
K			1300																			
Ca	30000-100000	60000	46700																			
V			<1			0,2	<1		0,2	<1		0,2	<1		0,2	<1		0,2	<1			0,2
Cr	**<100**	**5**	**4**			**3,4**	**4**		**3,4**	**4**		**3,5**	**4**		**3,4**	**4**		**3,7**	**4**			**3,4**
Fe	<300	<3	<5			5,3	<5		5,1	<5		4,9	<5		4,9	<5		5,1	<5			4,9
Mn	<300	<1	**<1**			**0,2**	**3**		**0,2**	**2**		**1,2**	**1**		**0,2**	**1**		**1,3**	**1**			**0,2**
Ni	**<100**	**4**	**11**			**10,9**	**12**		**11,1**	**12**		**11,7**	**12**		**10,9**	**12**		**12,1**	**12**			**11,4**
Cu	<1000	<1	<1			0,2	1		0,2	1		0,2			0,2	1		25,5	1			0,2
Mo			**26**			**24,4**	**28**		**24,6**	**28**		**25,2**	**27**		**25,1**	**28**		0,2	**27**			25,1
Zn	<5000	5	<10			1,2	<10		0,1	<10		0,3	<10		0,1	<10		**0,3**	<10			**0,4**
As	<10	<1	<1			0,2	<1		0,2	<1		0,2	<1		0,2	<1		0,2	<1			0,2
Se	<10	1	<2			0,4	<2		0,3	<2		0,3	<2		0,3	<2		0,3	<2			0,3
Sr			**204**			**252**	**210**		**252**	**211**		**250**	**212**		**250**	**214**		**250**	**212**			**253**
Ag	**200-500**	**300**	**400**	**310**	**350**	**231**	**13,7**	**23**	**0,4**	**0**	**0**	**0,05**	**2**	**0**	**0,06**	**2**	**0**	**0,06**	**1**	**0**		**0,05**
Cd			**0,1**			**<0,01**	**0,1**		**<0,01**	**0,1**		**<0,01**	**0,1**		**<0,01**	**0,1**		**<0,01**	**0,1**			**<0,01**
Sb			**0,1**			**0,04**	**0,1**		**0,04**	**0,1**		**0,05**	**0,1**		**0,04**	**0,1**		**0,04**	**0,1**			**0,04**
Ba	**<1000**	**10**	**10,4**			**10,4**	**10,6**		**10,5**	**10,5**		**10,4**	**10,8**		**10,4**	**10,5**		**10,1**	**10,8**			**10,5**
Hg	<2	0,1	<0,1			<0,1	0,1		<0,1	0,1		<0,1	0,6		<0,1			<0,1	0,1			<0,1
Pb	<50	2	<1			0,03	<1		0,02	<1		0,01	<1		0,01	<1		0,01	<1			0,01
U			**1,3**			**1,2**	**1,1**		**1,2**	**1,1**		**1,1**	**1,2**		**1,1**	**1,2**		**1,1**	**1,2**			**1,1**
W						**0,04**			**1,6**			**1,2**			**9,7**			**0,4**				**1,3**
F	**500-1500**	**1100**	910											817			885			879		
Cl	**<200000**	**1300**	1000		900			1630			619			2520			2810			1460		
NO3	**10000**	**5000**	4900																			
SO4	**250000**	**33000**	21000																			
I	<50	10																				
CN	<200	<10																				
NH4	<2000	30																				

Comments on the analysis of the first filling


TOC (microg/L)

•With regard of TOC, B series (acid passivated worse than A series (electropolyshed).

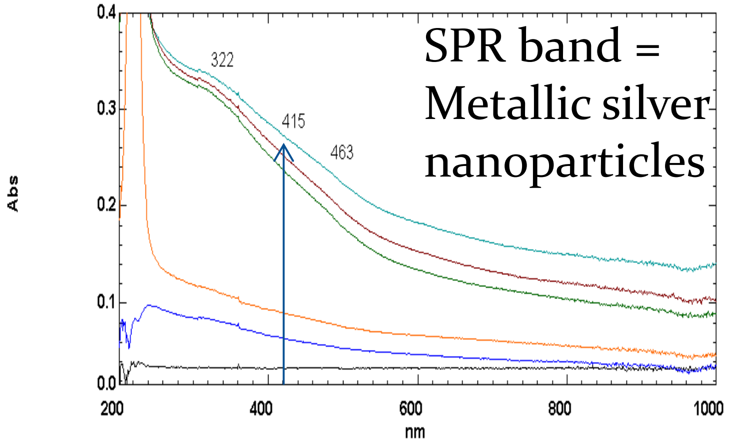
•On standing TOC increases with time case of tank 3A.

- After the first filling of all tanks at the original [Ag] = 400 µg/L, the silver vanished in one month.
- The analysis of LBC crosschecked between SMAT and CNR-IMC → no evidences on growth of [Fe], [Ni], [Mn] with the drop in [Ag].
- **Evidences on the growth of TOC = total organic carbon.**
- From previous study we know that all silver in LBC and HBC is in the form of ionic-colloidal. No metallic silver nanoparticles are present.
- Hypothesis: could be the release of TOC the cause of Ag reduction?

TOC could reduce colloidal Ag^+ to Ag^0

- Chromium carbides can be formed in 316L stainless steel during welding operations.
- The hydrolysis of chromium carbide releases hydrocarbons which increase the TOC and hydrogen (F.Cataldo, Int. J. Astrobiol. 2 (2003) 51-63).
- Hydrogen is able to reduce colloidal Ag^+ in LBC
- Acetylene is able to reduce colloidal Ag^+ in LBC

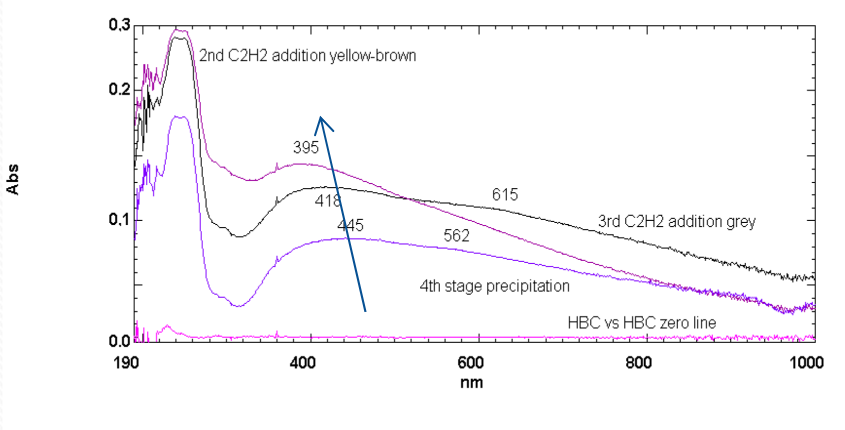
Reduction of HBC with H_2

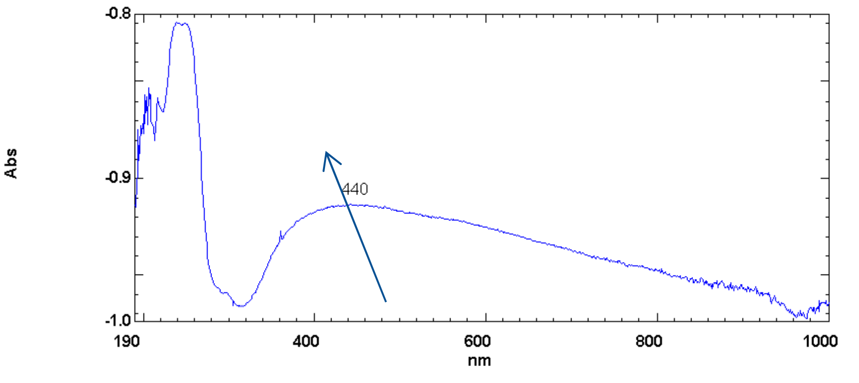


SPR band = Metallic silver nanoparticles

- Bubbling of H_2 in HBC causes the growth of the SPR band due to the formation of metallic silver nanoparticles.
- The colorimetric method is not able to detect metallic silver.
- Thus the reduction is confirmed by two methods, the growth of the SPR band and the lack of detection of silver with the colorimetric method.

Reduction of LBC & HBC with C_2H_2



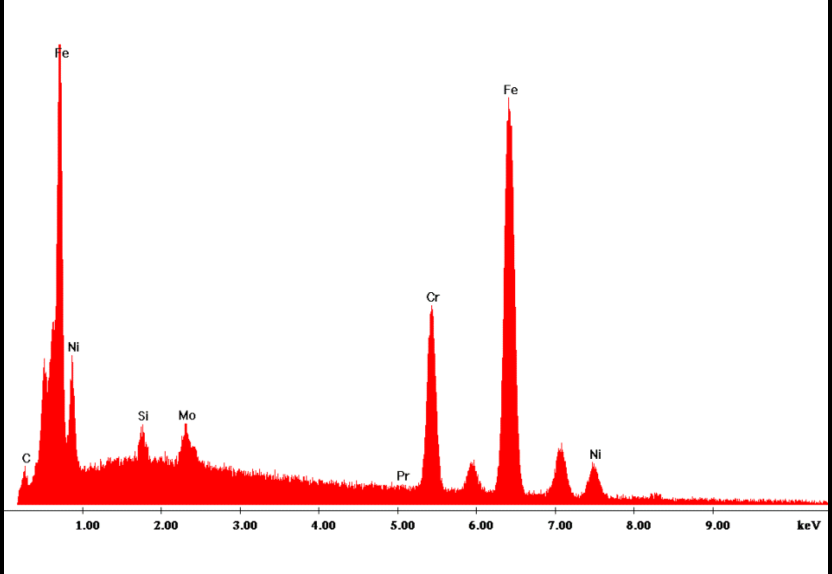


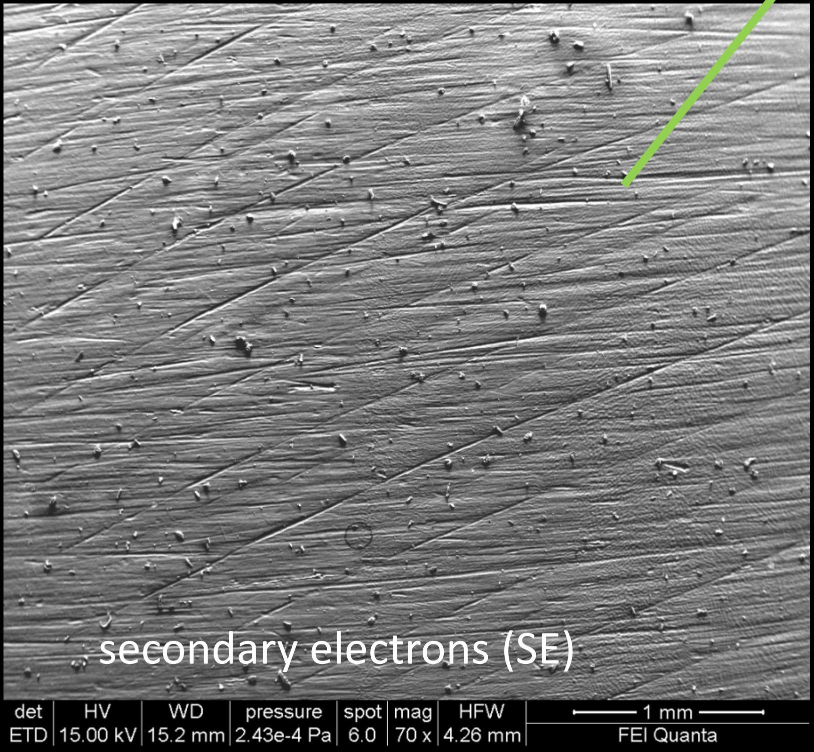
- Acetylene bubbling in HBC (upper figure) and LBC (lower figure) causes the reduction of Ag^+ in colloidal state to metallic silver nanoparticles

SEM = Scanning Electron Microscopy analysis of surfaces

1A CORPO0 SALDATURA

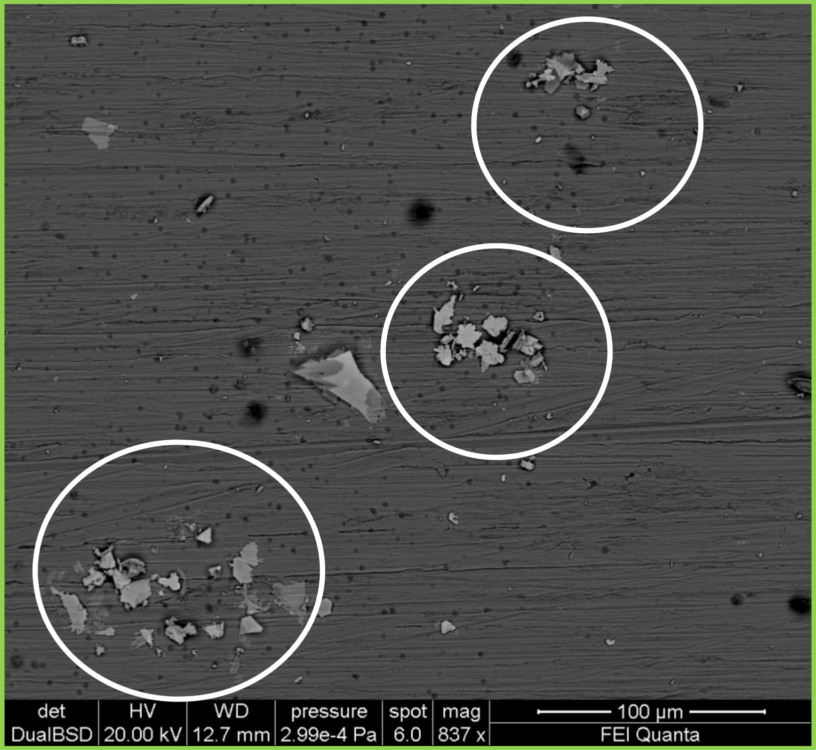
EDS-X RAY SPECTRUM GENERICO FONDO

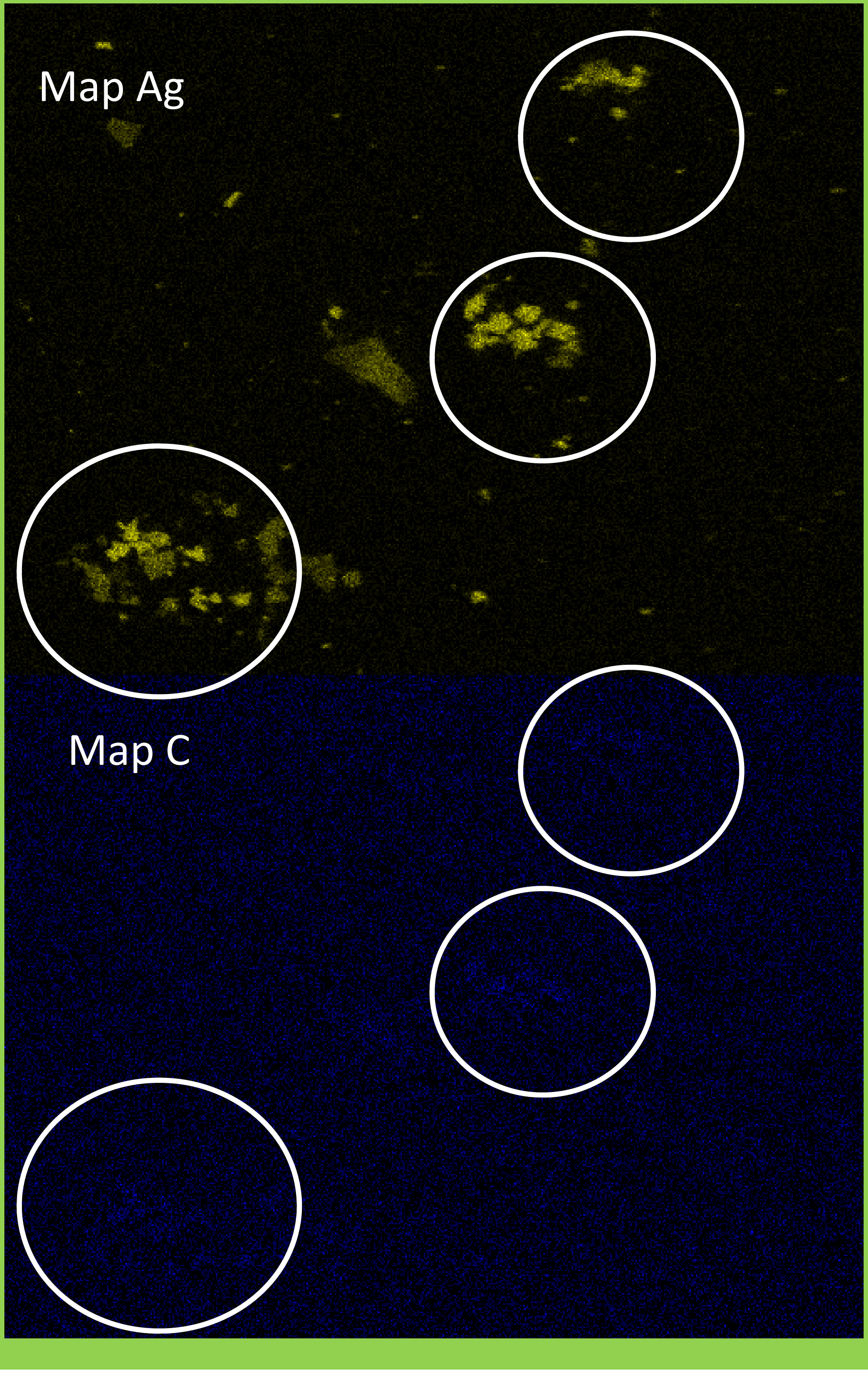




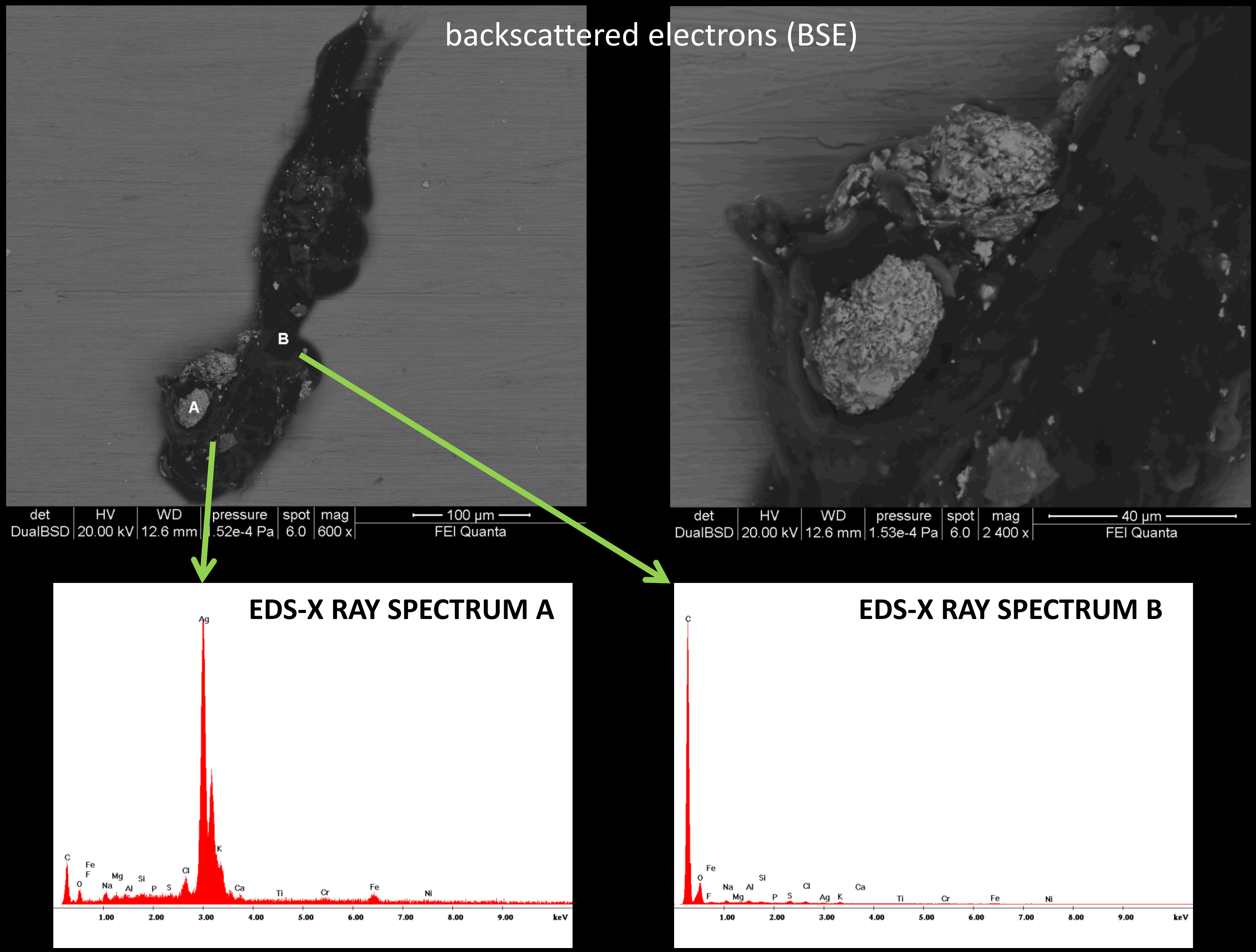
secondary electrons (SE)


1B CORPO 2


det
DualBSD
HV
20.00 kV
WD
12.7 mm
pressure
2.99e-4 Pa
spot
6.0
mag
837 x
100 µm
FEI Quanta


Map Ag
Map C

backscattered electrons (BSE)

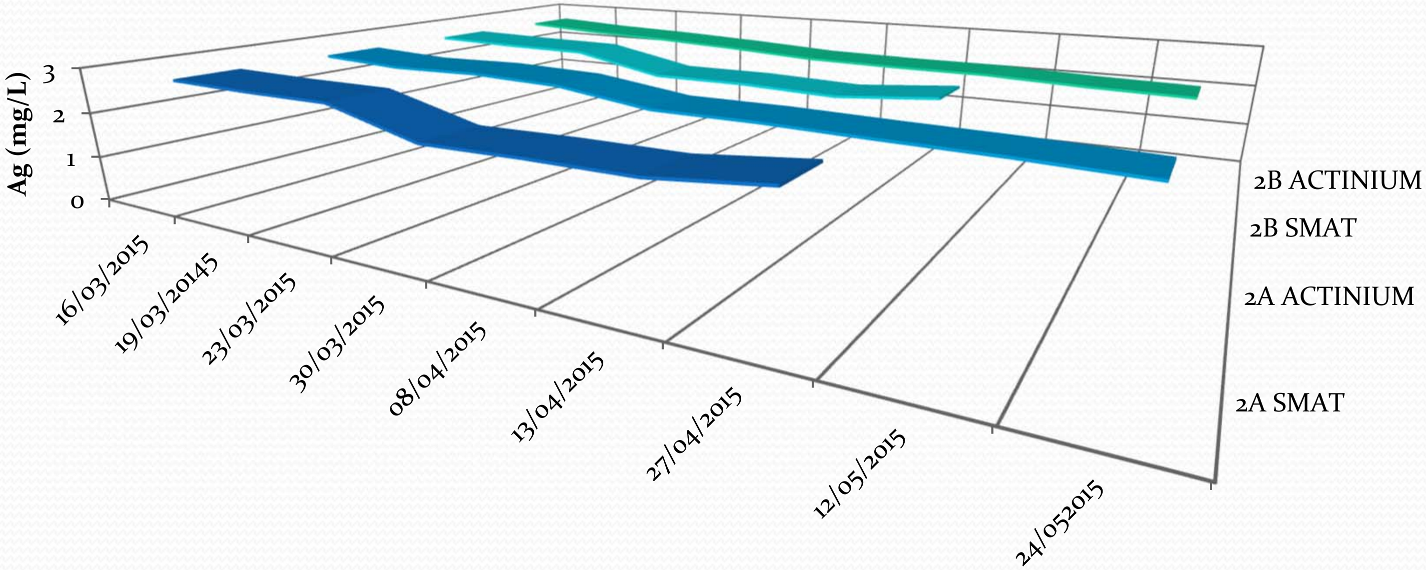


EDS-X RAY SPECTRUM A

EDS-X RAY SPECTRUM B

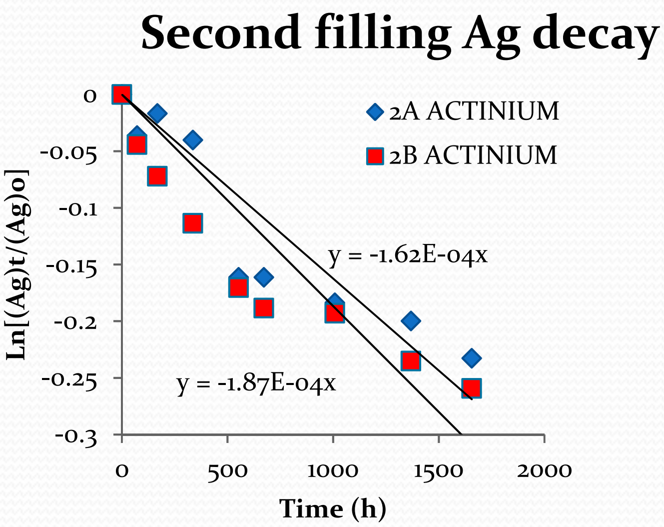
Summary of results after second filling

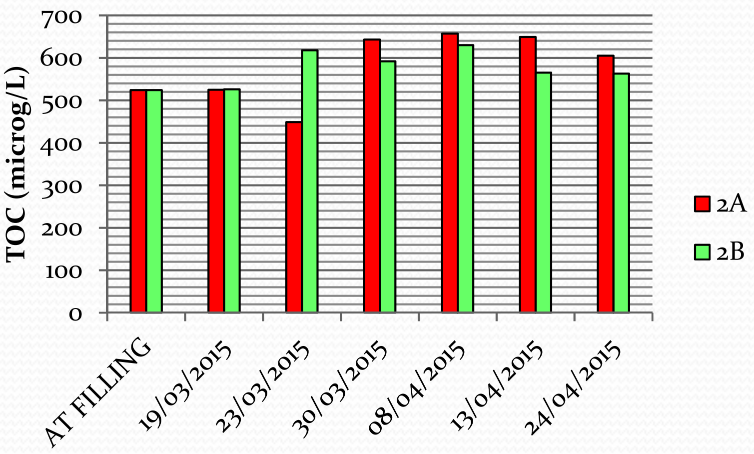
Summary of results of second filling



	16/03/2015	19/03/20145	23/03/2015	30/03/2015	08/04/2015	13/04/2015	27/04/2015	12/05/2015	24/052015
🟦 2A SMAT	2.644	2.62	2.63	2.10	2.14	2.14	2.36		
🟦 2A ACTINIUM	2.644	2.55	2.60	2.54	2.25	2.25	2.20	2.17	2.10
🟦 2B SMAT	2.644	2.60	2.58	2.15	2.15	2.07	2.26		
🟩 2B ACTINIUM	2.644	2.53	2.46	2.36	2.23	2.19	2.18	2.09	2.04

Comments on results of second filling





- Resonable agrement between SMAT and Actinium.
- Important fluctuations with time.
- Trend to slow Ag decay following pseudofirst order kinetics:

Electropolished k=1.6×10^{-4} h^{-1}

Acid passivated k=1.9×10^{-4} h^{-1}

- TOC shows a minimal increase and indeed the Ag decay is slow and minimal.

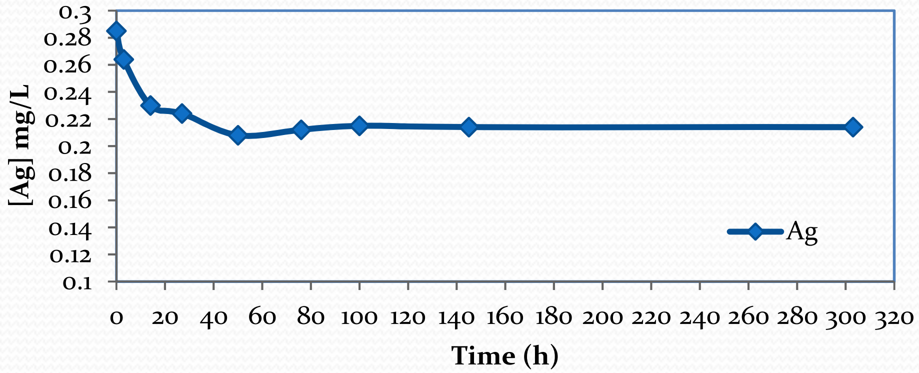
Second filling all analysis from SMAT

TANK	PROTOCOL	Sampling date	**Silver**	Aluminium	Arsenium	Boron	Barum	Cadmium	**Chromium**	Copper	**Iron**	Mercury	**Manganese**	**Molibdenum**	**Nichel**	Lead	Antimony	Selenium	Stronzium	Uranium	Vanadium	Zinc	TOC
			mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
AT FILL	4578	16/03/2015	**2,64**	nr	nr	nr	10,2	0,1	5	nr	nr	nr	nr	55	8	nr	0,9	nr	209	nr	nr	nr	524
2A	5168	19/03/2015	**2,62**	nr	nr	nr	10,3	0,2	5	nr	nr	nr	nr	55	9	nr	0,1	nr	213	nr	nr	nr	525
2B	5169	19/03/2015	**2,60**	nr	nr	nr	10,4	0,2	5	nr	nr	nr	nr	55	9	nr	0,1	nr	214	nr	nr	nr	526
2A	5170	23/03/2015	**2,63**	nr	nr	nr	10,4	0,2	5	1	nr	nr	nr	56	9	nr	0,1	nr	216	nr	nr	nr	449
2B	5171	23/03/2015	**2,58**	nr	nr	nr	10,5	0,2	5	nr	nr	nr	nr	55	9	nr	0,1	nr	215	nr	nr	nr	618
2A	5505	30/03/2015	**2,10**	nr	nr	nr	10,5	0,2	5	nr	nr	0,1	nr	56	7	nr	0,1	nr	208	1	nr	nr	643
2B	5506	30/03/2015	**2,15**	nr	nr	nr	10,4	0,2	5	nr	nr	nr	nr	56	8	nr	0,1	nr	207	1	nr	nr	592
2A	6389	08/04/2015	**2,14**	nr	nr	nr	10,7	0,2	5	nr	nr	0,1	nr	55	7	nr	0,1	nr	210	1	nr	nr	657
2B	6390	08/04/2015	**2,15**	nr	nr	nr	10,6	0,2	5	nr	nr	nr	nr	56	8	nr	0,1	nr	211	1	nr	nr	630
2A	6351	13/04/2015	**2,14**	nr	nr	nr	10,5	0,1	5	nr	nr	nr	nr	54	9	nr	0,1	nr	201	nr	nr	nr	649
2B	6352	13/04/2015	**2,07**	nr	nr	nr	10,4	0,1	5	1	nr	nr	nr	55	9	nr	0,1	nr	203	nr	nr	nr	565
2A	7595	27/04/2015	**2,36**	nr	nr	nr	10,4	0,1	5	nr	nr	nr	nr	55	8	nr	0,1	nr	207	nr	nr	nr	605
2B	7596	27/04/2015	**2,26**	nr	nr	nr	10,3	0,1	6	nr	nr	nr	nr	55	9	nr	0,1	nr	206	nr	nr	nr	563

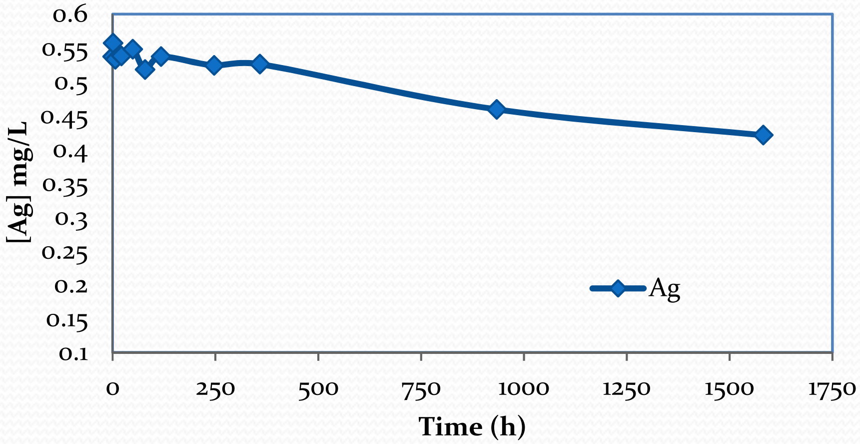
TESTS MADE ON TONGUES AND COUPONS

Ag decay in LBC on Ag^{1000} plate [S/V = 13 m^{-1}]

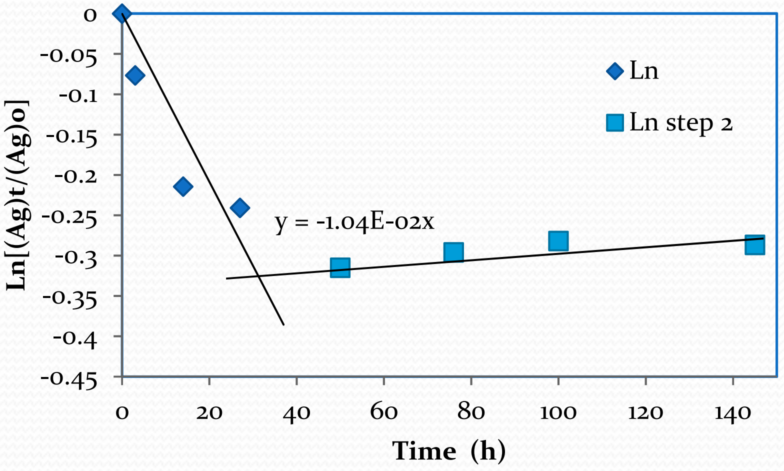
55-39 Ag^{1000} first run



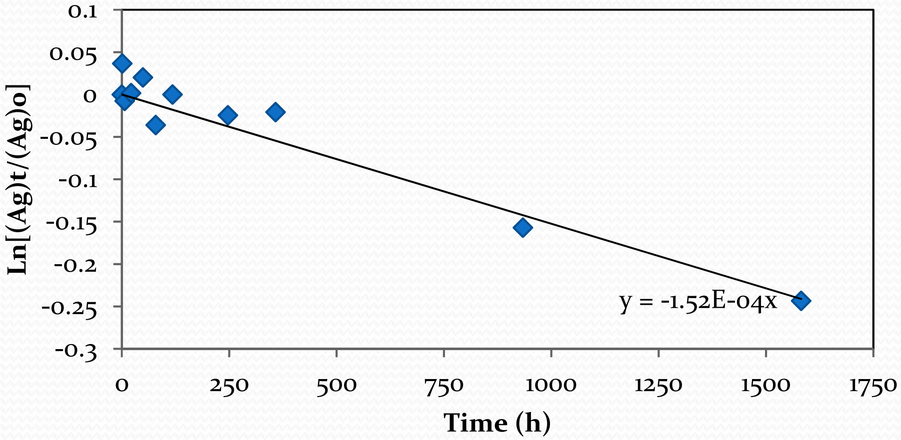
59-39 Ag^{1000} second run



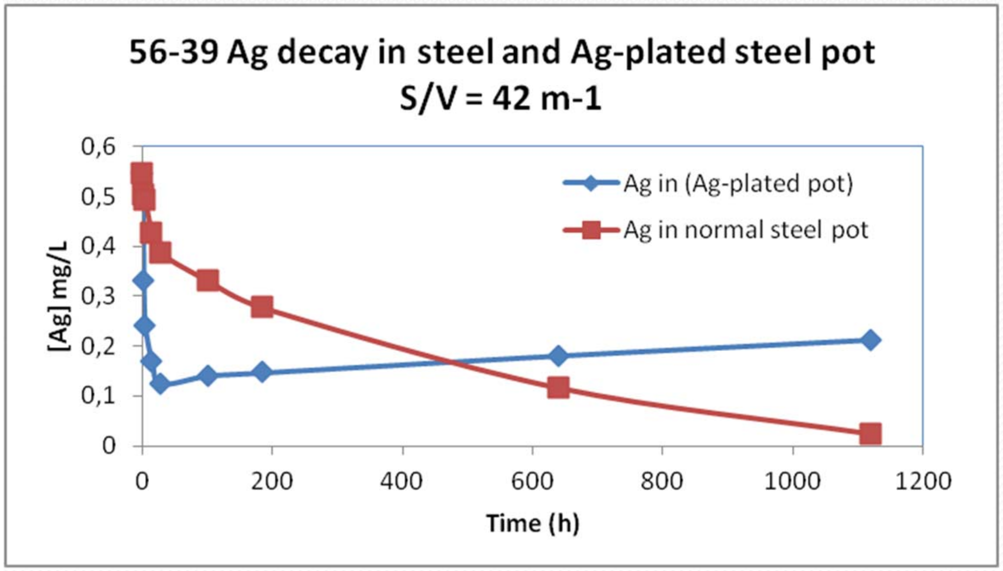
55-39 Ag^{1000} first run



59-39 Ag^{1000} second run



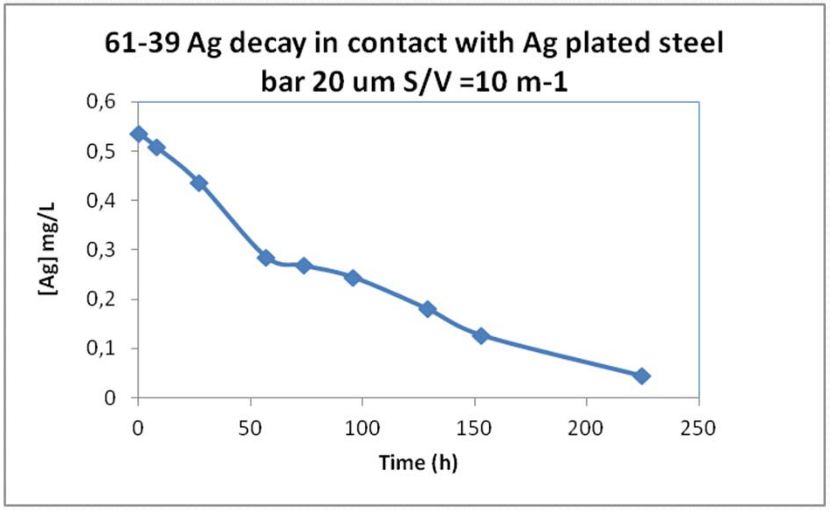
Ag decay in LBC on 316 steel pot and Ag plated steel pot S/V = 42 m^{-1}



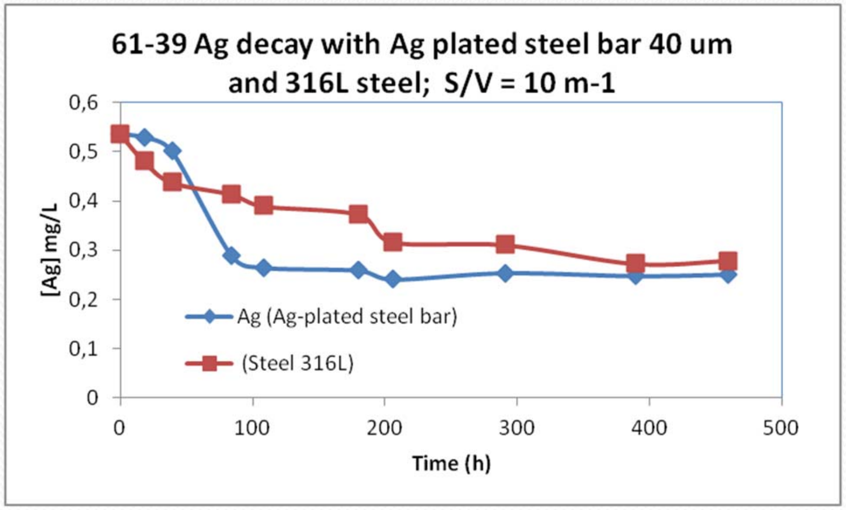
- The two pots half filled with LBC
- Initial rapid [Ag] decay in silver plated pot with some late recovery
- [Ag] decay to zero for AISI 316

Left pot = AISI 316
Right pot = Silver plated internally 20 micron Ag

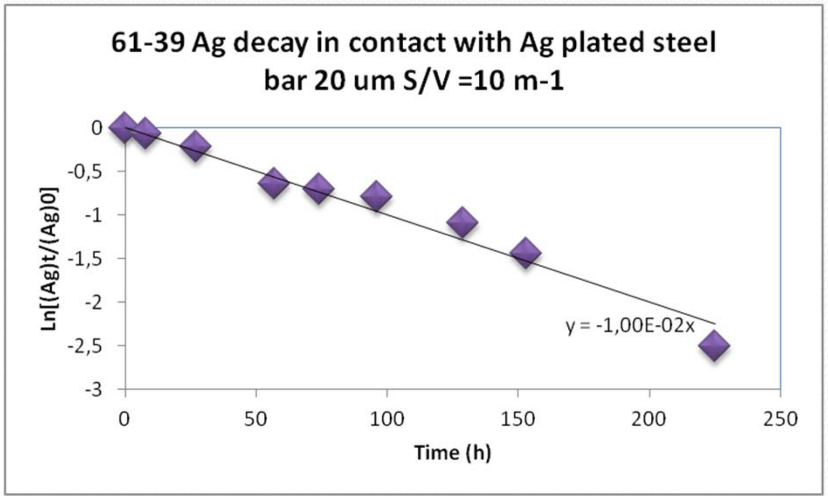
Silver plated 316L 20 and 40 micron against normal 316L commercial



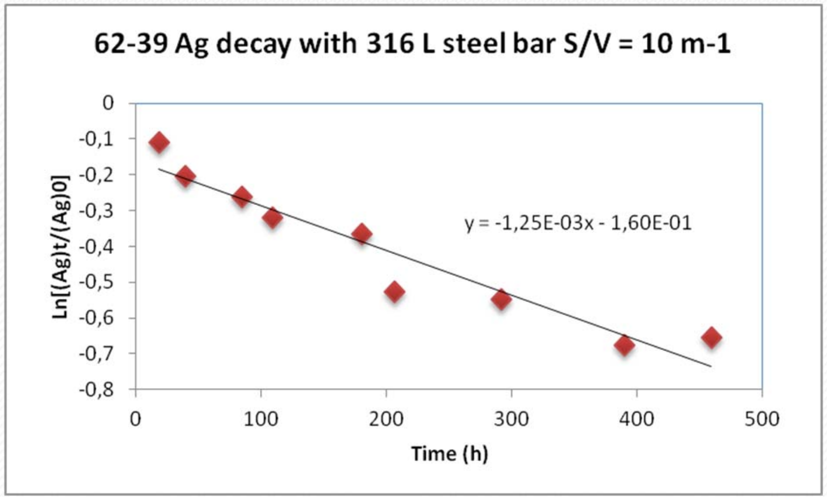
61-39 Ag decay in contact with Ag plated steel bar 20 um S/V =10 m-1



61-39 Ag decay with Ag plated steel bar 40 um and 316L steel; S/V = 10 m-1

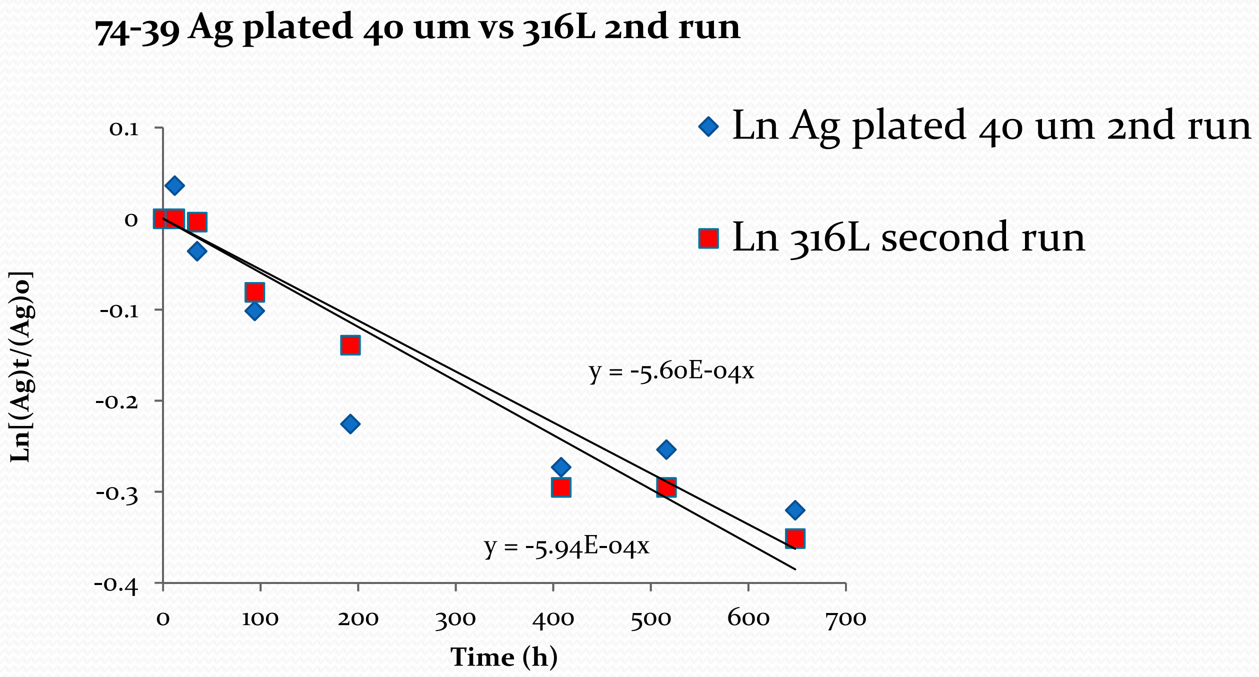


61-39 Ag decay in contact with Ag plated steel bar 20 um S/V =10 m-1

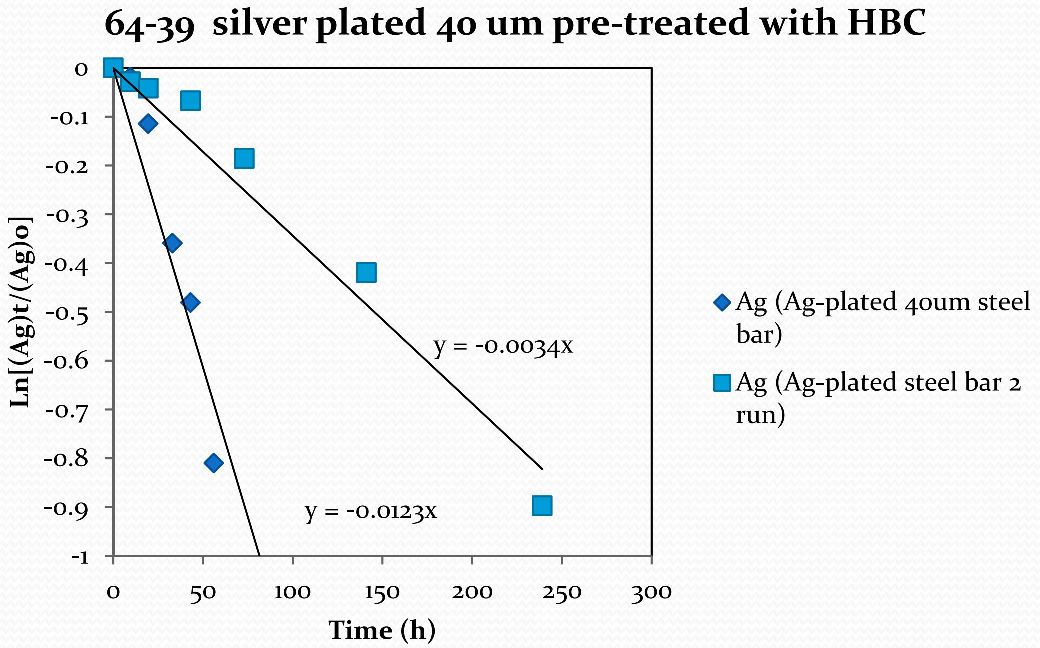


62-39 Ag decay with 316 L steel bar S/V = 10 m-1

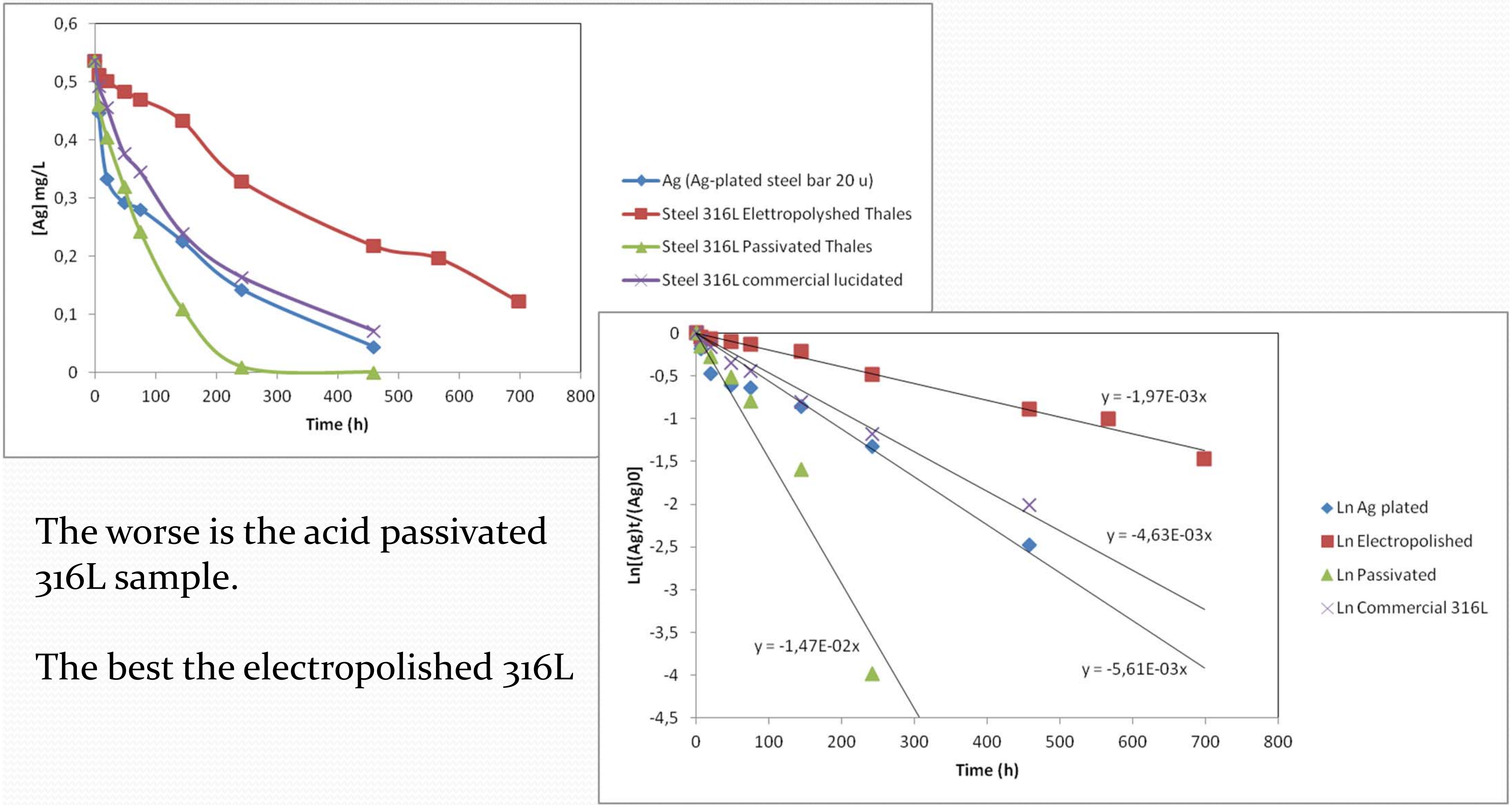
Ag decay in LBC on Ag plated 40 um steel bar previously treated with HBC ; S/V = 10 m^{-1}



Ag decay in LBC on Ag plated 40 um steel bar previously treated with HBC two run; S/V = 10 m^{-1}



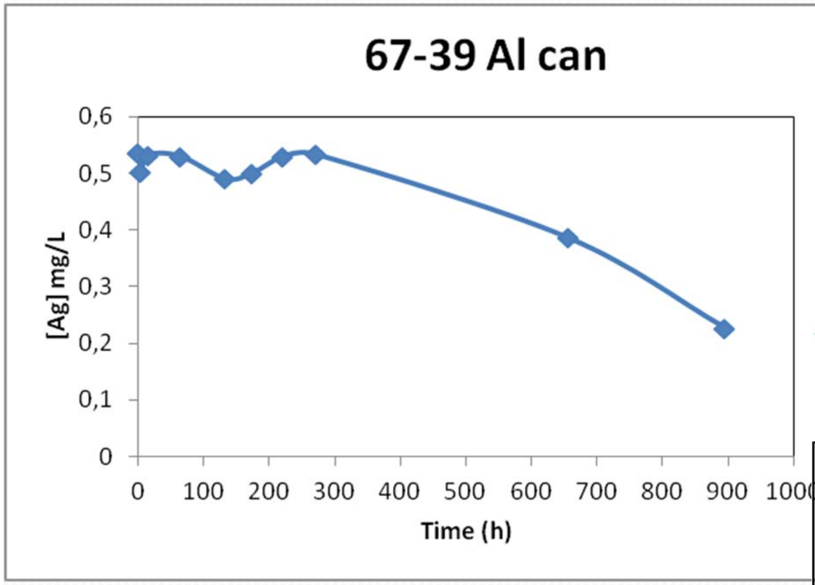
Ag decay in LBC on Ag plated 40 um steel bar and Thales 316 L bars



The worse is the acid passivated 316L sample.

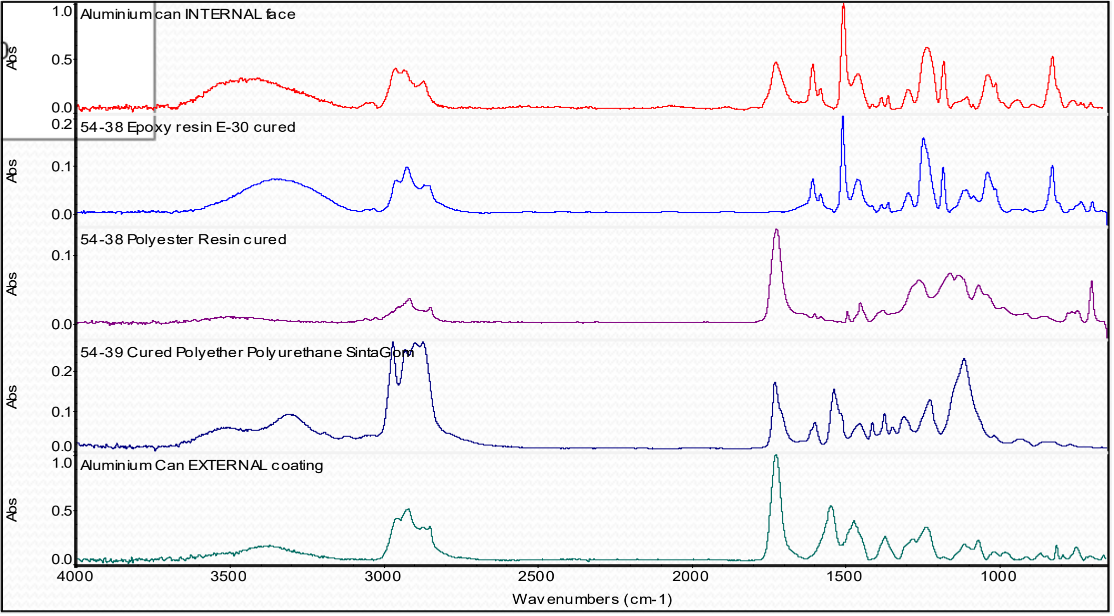
The best the electropolished 316L

Aluminium can with LBC water: Incredible performance S/V = $74m^{-1}$



Stable to LBC for > 300 h with unfavorable S/V !!!

The secret? A very thin epoxy coating Inside the can. Below the infrared spectra: red trace epoxy coating blue trace reference epoxy spectrum

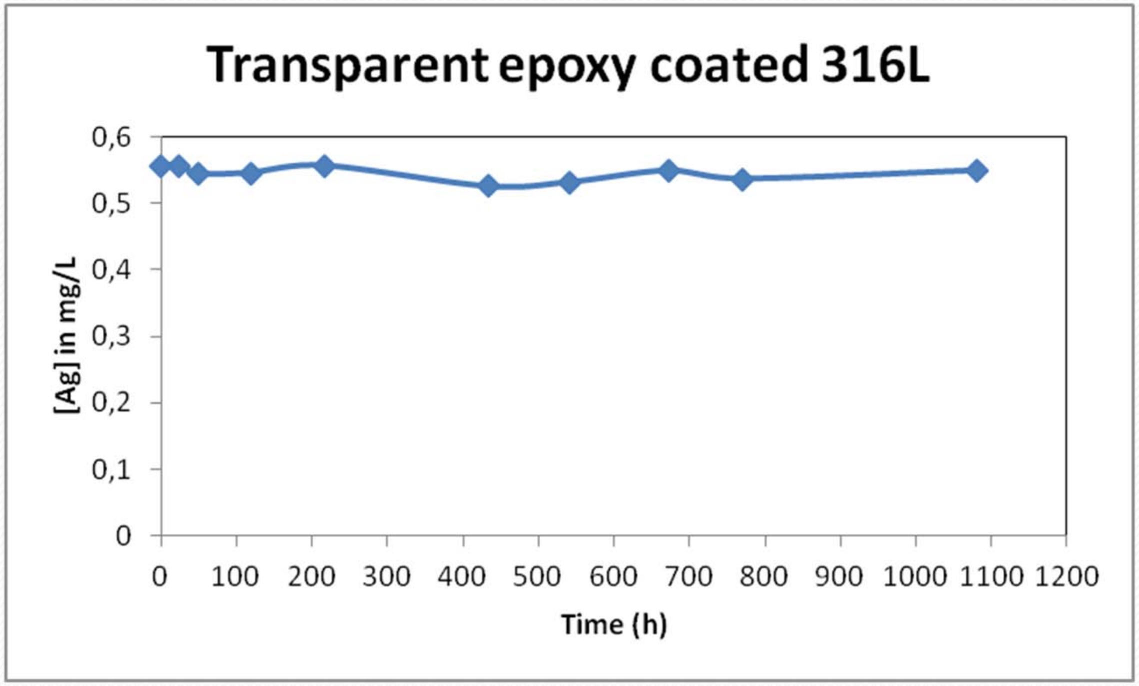


Prepared 316L coated with epoxy resin suitable for food contact

From top to bottom of the picture:

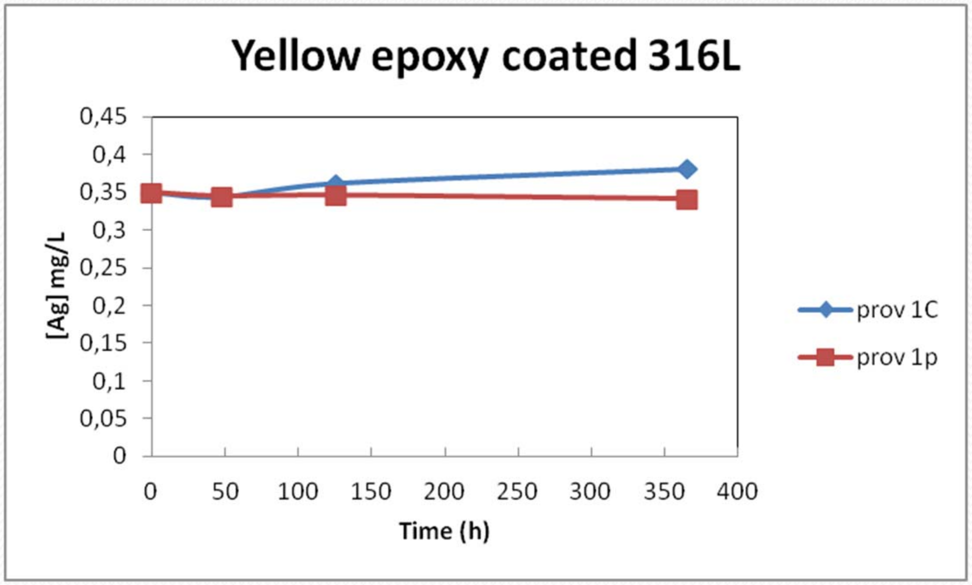
1. **Steel 316L with yellow epoxy coating**
2. **Steel 316L with transparent epoxy coating**
3. Steel 316L commercial pristine
4. Steel 316L Ag plated 40 micron

Results with transparent epoxy-coated 316L: It works!!!



More than 1000 h at S/V = 10 m^{-1} no decay in [Ag]

Results with yellow epoxy-coated 316L: It works!!!



Excellent results also with yellow epoxy coated 316L with LBC; the test is still running.

It is normal industrial practice to cover the steel tanks for water or beer, wine and other alcoholic beverages with a coating of epoxy resin suitable for food contact According to the EU legislation.

Summary of kinetics measurements

Run	**Metal surface**	**S/V (m^{-1})**	**[Ag] initial**		**k (h^{-1})**
55-39	Ag1000	13	0.285	k(0-30h)= -0,0104	**constant > 300h**
59-39	Ag1000	13	0.537	k(0-400h)= constant	k(400-00 h)= -1.48x10^{-4}
61-39	316L Ag plated 20 um	10.2	0.547		-1.0x10^{-2}
62-39	316L Ag plated 40 um	10.2	0.547	k(0-100h) = -2,74x10^{-3}	k(100-00 h) = constant
74-39	316L Ag plated 40 um 2nd run	10.2	0.547		-5.6x10^{-4}
64-39	316L Ag plated 40 um	10.2	0.547		-1.23X10^{-2}
64-39	316L Ag plated 40 um 2nd run	10.2	0.547		-3.43x10^{-3}
62-39	316L commercial	10.2	0.547		-1.25x10^{-3}
74-39	316L commercial 2nd run	10.2	0.547		-5.94x10^{-4}
73-39	316L Ag plated 20 um	25.5	0.547		-5.61x10^{-3}
73-39	Electropolished	25.5	0.547		-1.97x10^{-3}
73-39	Acid Passivated	25.5	0.547		-1.47x10^{-2}
73-39	316L Commercial	25.5	0.547		-4.63x10^{-3}
tank 2A	Electropolished	24.5	2.64		-1.62x10^{-4}
tank 2B	Acid passivated	24.5	2.64		-1.87x10^{-4}
67-39	Aluminium can epoxy coated	74	0.537	k(0-300) = constant	
72-39	**316L comm transp epoxy coated**	**10.2**	**0.547**		**constant > 1100 h**
83-39	**316L comm yellow epoxy coated**	**9.6**	**0.35**		**constant > 400 h**
APPENDIX					
52-39	Ag800	77.7	0.285		-0.14
58-39	Ag800	77.7	0.547		-0.247
52-39	Food steel 316L	62	0.285		-4.68x10^{-3}
56-39	Pot Ag plated 20 um	42	0.547	k(0-5h)= -0.253	k(5-00h)= -8.19x10^{-5}
56-39	Pot steel 316L	42	0.547		-2.84x10^{-3}

Comments on kinetics measurements

- Silver plating of 316L steel needs a previous Ni deposition on steel followed by silver deposition.
- At 20 and 40 µm silver thickness there are no decisive advantages over electropolished 316L steel.
- Even pure silver 1000 plate adsorbs silver from LBC !
- Among the coupons tested electropolished 316L is the best followed by commercial 316L sample while acid passivated is the worse.
- Based on kinetics measurements, it looks like the tanks A series (nominally electropolished) had the same surface treatment as the B series (nominally acid passivated).

Special recommendations

- Epoxy coating of the internal surface of the 316L tank could be a radical and definitive solution for the interaction between LBC and the steel surface.

- Internal epoxy coating is an industrial standard practice for steel tanks which must contain beer, wine, beverages in general.

- Internal epoxy coating is also a standard practice for internal coating of aluminium can designed for beer and general beverages.

- The use of epoxy coating inside steel tanks and Al cans is permitted by law.

- **Our study has shown that LBC concentration remains stable even after >1100 h at $S/V = 10\ m^{-1}$. Thus, no adsorption at all of ionic colloidal silver on the epoxy coating.**

Summary of the LBC in FEP bottles

	ACTINIUM	ACTINIUM	SMAT	SMAT	ACTINIUM	ACTINIUM	ACTINIUM
	FEP-1	FEP-2	FEP-1	FEP-2	FEP-3	FEP-4	FEP-5
03/02/2015	0.290						
24/02/2015	0.280	0.280					
18/04/2015	0.285	0.272	0.237	0.237	0.281	n.d.	n.d.
24/05/2015	cut	0.282			0.295	0.320	0.299

Comments: in FEP bottles the concentration of LBC remains completely stable for months.

FEP is a suitable material for LBC.

We will cut and study the surface of FEP bottle which has contained LBC for months.

Appendix

STEEL CORROSION WITH SILVER

The main components of the stainless steel AISI 316L, which are ≈18% of chromium, ≈8% of nickel and ≈69% of iron. The chemical equilibria occurring in such conditions can be depicted as follows:

$2Ag^+ + Fe \rightarrow Ag + Fe^{2+}$ (1)
$2Ag^+ + Ni \rightarrow 2Ag + Ni^{2+}$ (2)
$3Ag^+ + Cr \rightarrow 3Ag + Cr^{3+}$ (3)

For each of the above chemical equilibrium we can apply the Nernst equation (67-72):

$E_{Ag+/Ag} = E°_{Ag+/Ag\,+}\ RT/2F\ Ln[Ag^+]^2$ (1')
$E_{\ Fe2+/Fe} = E°_{Fe2+/Fe} + RT/2F\ Ln[Fe^{2+}]$ (1")
$E_{Ag+/Ag} = E°_{Ag+/Ag} + RT/2F\ Ln[Ag^+]^2$ (2')
$E_{\ Ni2+/Ni} = E°_{Ni2+/Ni} + RT/2F\ Ln[Ni^{2+}]$ (2")
$E_{Ag+/Ag} = E°_{Ag+/Ag} + RT/3F\ Ln[Ag^+]^3$ (3')
$E_{Cr3+/Cr} = E°_{Cr3+/Cr} + RT/3F\ Ln[Cr^{3+}]$ (3")

Silver ions could corrode steel

TABLE 1 - OXIDIZING POWER OF Ag^+ AGAINST STAINLESS STEEL

		Volt	LnK	K (298 Kelvin)
eq. 1' - 1"	E_{Ag}-E_{Fe} (*)	1.146	89.2	5.5×10^{38}
eq. 1' - 1"	E_{Ag}-E_{Fe} (**)	1.128		
eq. 2'- 2"	E_{Ag}-E_{Ni} (*)	1.367	159.6	2.1×10^{69}
eq. 2'- 2"	E_{Ag}-E_{Ni} (**)	1.349		
eq. 3'- 3"	E_{Ag}-E_{Cr} (*)	0.901	70.1	2.9×10^{30}
eq. 3'- 3"	E_{Ag}-E_{Cr} (**)	0.883		

- Thermodynamics calculations through the Nernst’s equation suggest that the corrosion is possible

Nature of silver in flight water

- If silver is predominantly or exclusively under the form of colloidal metallic nanoparticles, then it is already in a reduced form and the electrochemical reactions 1-3 cannot occur. Consequently, in this condition, silver can undergo only a physical adsorption on the steel surface whereas a silver metallic nanoparticle is deposited on the steel surface.
- If instead silver in flight water is predominantly or exclusively in ionic form (as we have verified it is the real case), then the electrochemical reactions 1-3 should occur leading to the deposition of metallic silver on the steel surface with the oxidation and solubilization of the metals composing the steel alloy.

GALVANIC CORROSION FOR NON-UNIFORM SILVER DEPOSITION

- In the case of metallic silver deposition either as metallic nanoparticles or as electrochemical deposits from ionic silver, we will have the condition of a non-uniform silver deposit on the steel surface. This is a condition in which we have two different electrodes Ag and Fe in a shortcut leading to a galvanic corrosion due to a metal couple.

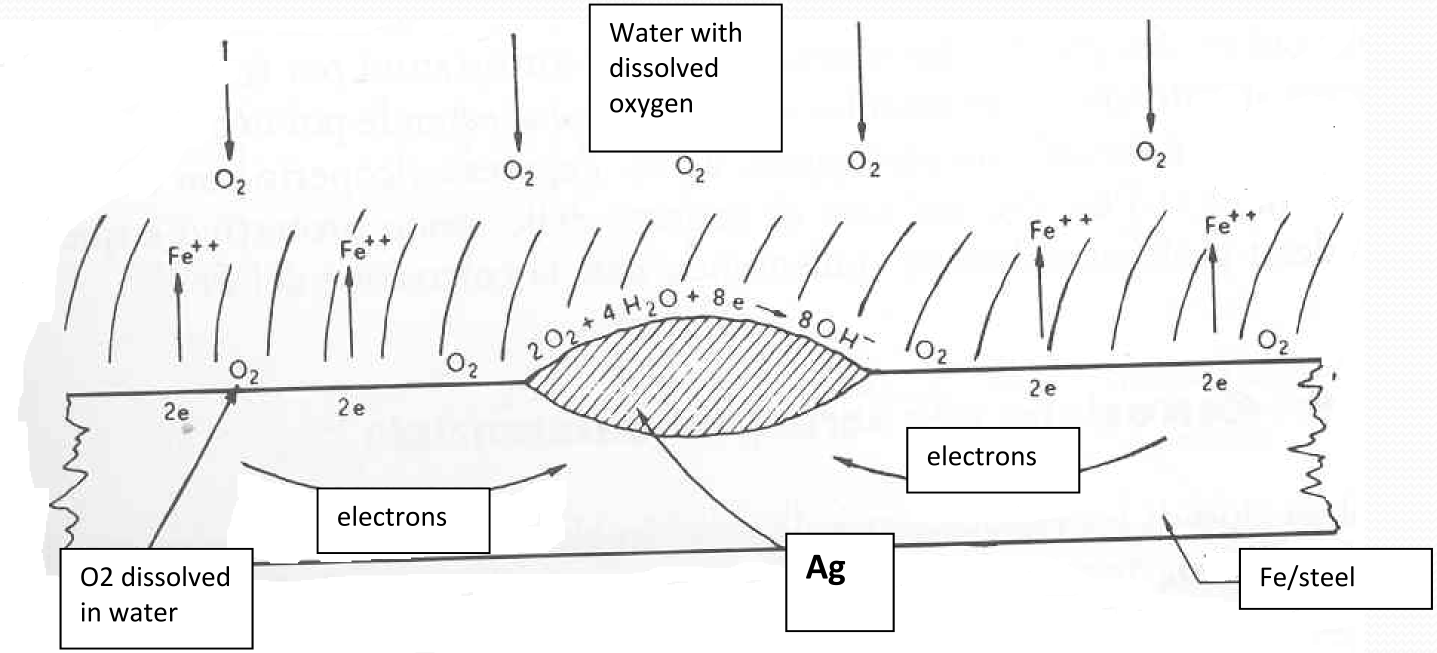
- Since Fe^{2+}/Fe ($E° = -0.447$ V) and Ag^{+}/Ag ($E° = +0,799$ V), Fe will be oxidized and will pass into solution as Fe^{2+} releasing 2 electrons which will migrate on the Ag domain.

- On the surface of Ag it will occur the reduction of water dissolved oxygen according to the reaction:

  $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

and this reaction is favored by an $O_2/4OH^-$ $E° = +0.401$ V.

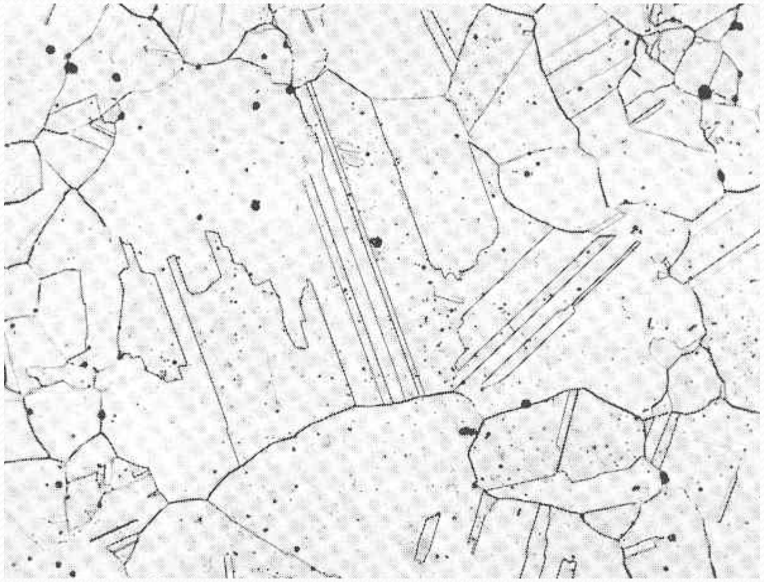
Model of Galvanic corrosion



The consequence of such a reaction will be a gradual increase in the pH of the water solution which may also cause the precipitation of Fe^{2+} as $Fe(OH)_2$ which is insoluble. The subtraction of Fe^{2+} from the solution will cause a further oxidation of other Fe from the steel surface giving dynamicity to the corrosion process.

Appendix 2

About stainless steel 316L



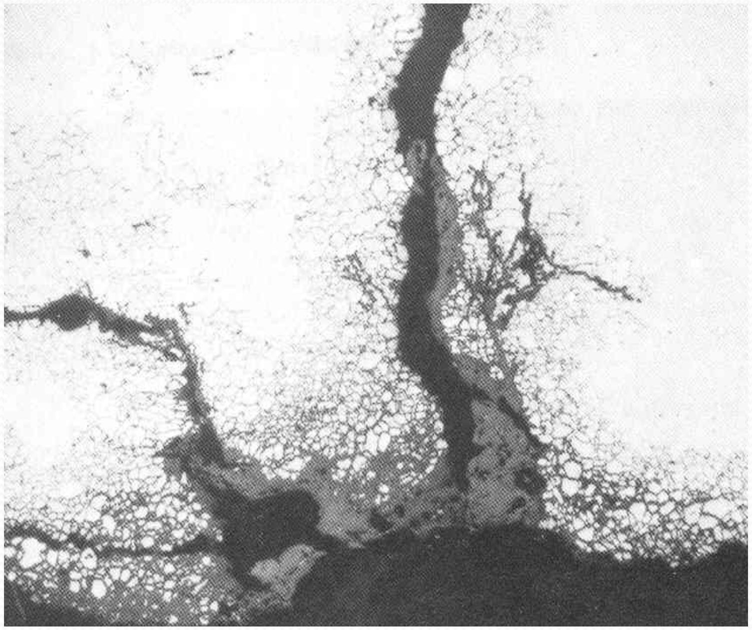
Austenite morphology

- A crystalline modification of iron is iron γ whose field of existence is comprised between 911°C and 1392°C and is characterized by a cubic face-centered crystalline lattice. This phase is known as Austenite.
- It is possible to expand the field of existence of Austenite even to room temperature when iron is added with Ni, Mn, Cu, C and N.

About stainless steel 316L

- Alloy 316/316L (UNS S31600/S31603) is a chromium-nickel-molybdenum austenitic stainless steel developed to provide improved corrosion resistance to Alloy 304/304L.
- It is common practice for 316L to be dual certified as 316 and 316L. The low carbon chemistry of 316L combined with an addition of nitrogen enables 316L to meet the mechanical properties of 316.
- Alloy 316/316L resists atmospheric corrosion, as well as, moderately oxidizing and reducing environments. It also resists corrosion in polluted marine atmospheres. Alloy 316/316L has excellent strength and toughness at cryogenic temperatures.

Drawbacks of 316



Intergranular corrosion in an Austenitic stainless steel

- **Sensitivity to the intergranular precipitation of carbides**
- The precipitation of chromium carbides occurs by more or less prolonged heating of the Austenitic steel between 500 and 800°C for example during welding operations.
- The interganular precipitation of chromium carbides from one side causes a reduction of the chromium concentration in the austenitic matrix and the accumulation of this chemical specie just at the interface of the granules
- Once such thermally treated steel is exposed to moderately corrosive environments the precipitated chromium carbides are preferentially attacked and hydrolyzed causing a corrosion between the granules

How to reduce intergranular corrosion

- The steel is defined “sensitized” when there is precipitation of Cr-Carbides.
- To reduce the intergranular corrosion it is necessary another thermal treatment to solubilize the chromium carbides or, alternatively, it is necessary to use steels with very low carbon content ($C < 0.03\%$, L-series)