

## Supplemental Material

### Metal bioaccessibility in synthetic body fluids – a way to consider positive and negative alloying effects in hazard assessments

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**Content:** Tables S1- S4; Figures S1-S4

#### S1 Methods

##### S1.1 Metal release measurements

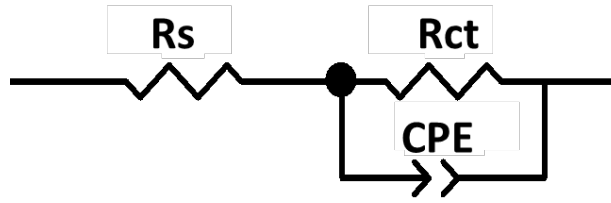
Calibration of the measurement using flame-AAS or GF-AAS was made using 1% ultrapure HNO<sub>3</sub> and three or four metal standard concentrations (10, 30, 100 µg/L for Ni, and 10, 30, 60, 100 µg/L for Co for GF-AAS; 1, 3, 10 mg/L for Ni, and 1, 3, 10, 30 mg/L for Co for flame-AAS). Recalibration was done in the case of a calibration curve correlation coefficient less than 0.995. The detection limits were 1.32 µg Ni/L and 0.74 µg Co/L using GF-AAS, and 0.035 mg Ni/L and 0.40 mg Co/L using flame-AAS, as estimated based on three times the average standard deviation of the blank samples. Quality control samples of known concentrations were analyzed every 5<sup>th</sup> sample to ensure accurate analysis, all showing acceptable ( $\pm 10\%$ ) values. Sample concentrations exceeding the calibration range were re-analyzed in a diluted form (diluent 1% ultrapure HNO<sub>3</sub>) or in the flame mode. Samples with metal concentrations lower than the limits of detection were denoted as <LOD.

##### S1.2 Electrochemical impedance spectroscopy (EIS)

The EIS data was fitted by ZView software using a one-time constant equivalent circuit (Figure S1). In this model,  $R_s$  is solution resistance between working and reference electrode,  $R_{ct}$  is the charge transfer or polarization resistance, and CPE (constant phase element) represents the double layer capacitance along the electrode surface, which is non-ideal as a result of surface inhomogeneity, roughness, edge effects, etc.

The impedance of the CPE ( $Z_{CPE}$ ) is defined as  $Z_{CPE} = 1/(Q(j\omega)^n)$ , where  $Q$  is a constant representative for the CPE,  $j$  is the imaginary unit ( $j^2 = -1$ ),  $\omega$  is the angular frequency and  $n$  ( $0 \leq n \leq 1$ ) is the phase constant exponent [1]. The effective capacitance ( $C_{eff}$ ) for each system was calculated using the formula [2],

$$C_{eff} = [Q(\frac{1}{R_{ct}} + \frac{1}{R_s})^{(n-1)}]^{1/n}$$



*Figure S1. Equivalent circuit used for EIS data fitting in ZView software (for all specimens).  $R_s$ , solution resistance;  $R_{ct}$ , charge transfer or polarization resistance; and  $CPE$ , constant phase element.*

## S2 Results and Discussions

### S2.1 Surface oxide (XPS)

Table S1. Relative mass concentrations (wt.%) of metallic (met) and oxidized (ox) peaks of the main alloying metals within the outermost surface oxide by means of XPS of the investigated alloys (stainless steels – 304, 316, 430 and LDX2101; low-alloyed steel) prior to (unexposed-Un) and exposed to ASW, ASL and GST for 168 h; relative ratio (wt.%) of oxidized to the sum of metallic and oxidized peaks. This relative ratio gives information on the relative oxide thickness – if greater, the oxide is thicker, and if 100%, the oxide is thicker than the detection depth of the instrument (5-10 nm). Average values and standard deviation of independent duplicate coupons (each measured twice at different surface locations). <LOD – below limit of detection

Grade	Exposure	Ni (wt.%)	Fe (wt.%)		Cr (wt.%)		$\frac{(\text{Ni}+\text{Fe}+\text{Cr})_{\text{ox}}}{(\text{Ni}+\text{Fe}+\text{Cr})_{\text{ox}+\text{met}}}$ (wt./wt. %)
		met	met	ox	met	ox	
304	Un	1.1 ± 0.4	5.1 ± 0.05	32 ± 1.0	1.2 ± 0.01	11 ± 0.1	85 ± 0.3
	ASL	<LOD	0.68 ± 0.4	18 ± 0.3	0.25 ± 0.4	5.4 ± 0.5	96 ± 2.9
	ASW	0.80 ± 0.5	2.1 ± 0.04	23 ± 0.2	0.54 ± 0.08	11 ± 0.6	91 ± 1.1
	GST	1.5 ± 0.1	4.5 ± 1.4	11 ± 1.9	1.1 ± 0.1	24 ± 0.2	83 ± 3.6
316L	Un	0.65 ± 0.2	3.1 ± 0.07	29 ± 1.2	0.61 ± 0.2	9.3 ± 0.6	90 ± 1.4
	ASL	<LOD	0.23 ± 0.3	18 ± 2.5	<LOD	3.8 ± 0.5	99 ± 1.3
	ASW	1.1 ± 0.3	3.1 ± 0.1	22 ± 2.2	0.66 ± 0.08	9.4 ± 0.3	87 ± 1.6
	GST	1.3 ± 0.1	2.9 ± 0.2	9.0 ± 1.2	0.40 ± 0.6	20 ± 0.1	87 ± 0.6
430	Un	<LOD	4.5 ± 0.07	29 ± 0.04	1.3 ± 0.5	10 ± 0.3	87 ± 1.1
	ASL	<LOD	<LOD	20 ± 1.5	<LOD	3.0 ± 1.1	100
	ASW	<LOD	5.1 ± 0.6	37 ± 1.0	0.92 ± 0.08	11 ± 0.5	89 ± 1.2
	GST	<LOD	<LOD	<LOD	1.0 ± 0.07	40 ± 1.1	97 ± 0.1
LDX2101	Un	<LOD	5.5 ± 0.09	31 ± 0.1	1.3 ± 0.02	12 ± 0.9	86 ± 0.5
	ASL	<LOD	<LOD	17 ± 0.2	<LOD	3.4 ± 0.4	100
	ASW	<LOD	3.6 ± 0.17	30 ± 0.5	1.0 ± 0.02	10 ± 0.4	90 ± 0.08
	GST	<LOD	5.7 ± 1.4	11 ± 0.1	<LOD	23 ± 1.3	85 ± 2.0
Low alloyed steel	Un	<LOD	3.6 ± 0.05	34 ± 1.4	<LOD	<LOD	91 ± 0.2
	ASL	<LOD	<LOD	51 ± 6.0	<LOD	<LOD	100
	ASW	<LOD	2.2 ± 0.08	51 ± 1.0	<LOD	<LOD	96 ± 0.2
	GST	<LOD	<LOD	41 ± 4.5	<LOD	<LOD	100

## S2.2 Corrosion resistance

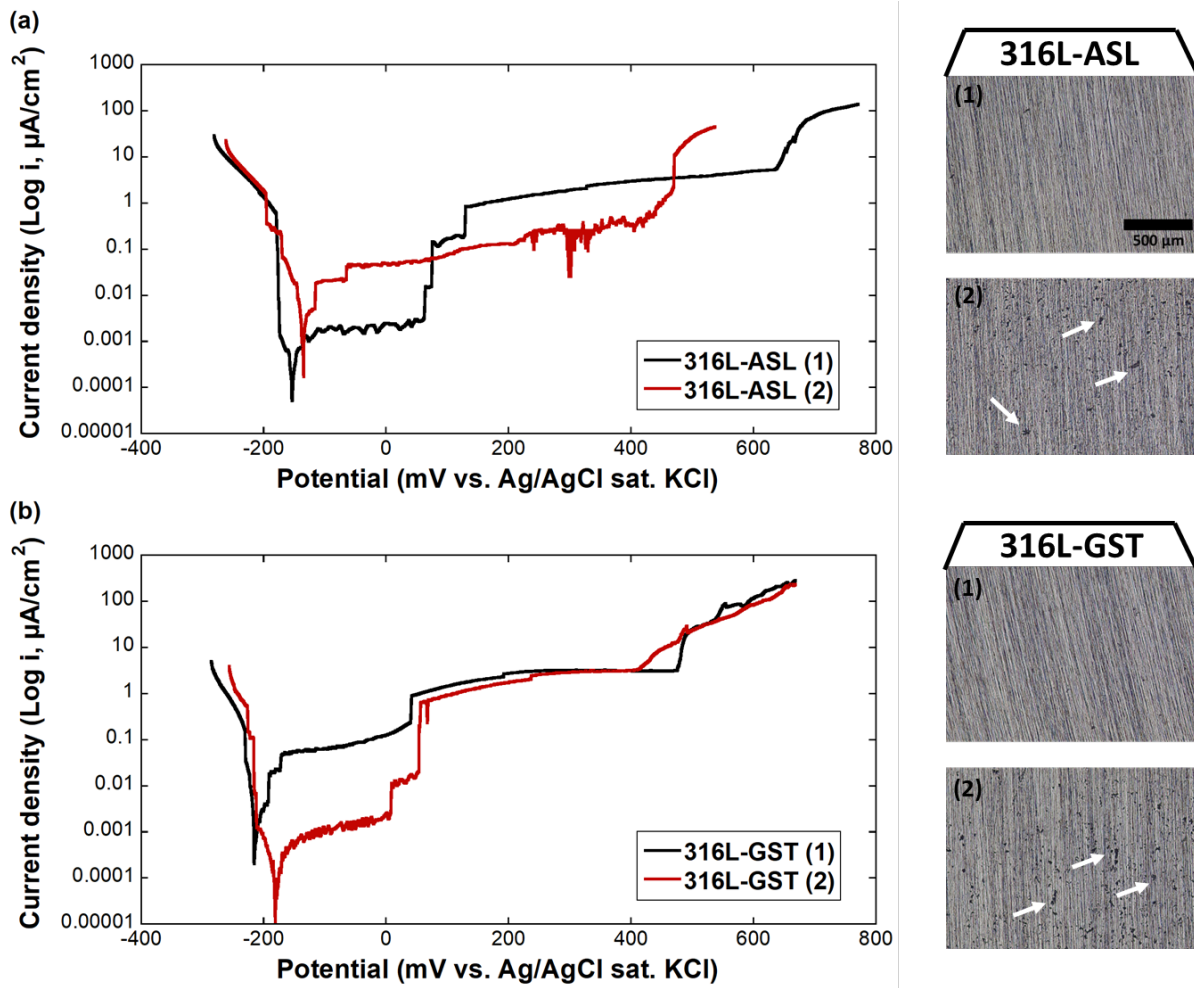


Figure S2. Current density – potential curves of duplicate coupons of stainless steel grade 316L exposed to (a) ASL (pH 6.75) and (b) GST (pH 1.5), and corresponding post-polarization LOM images (same magnification).

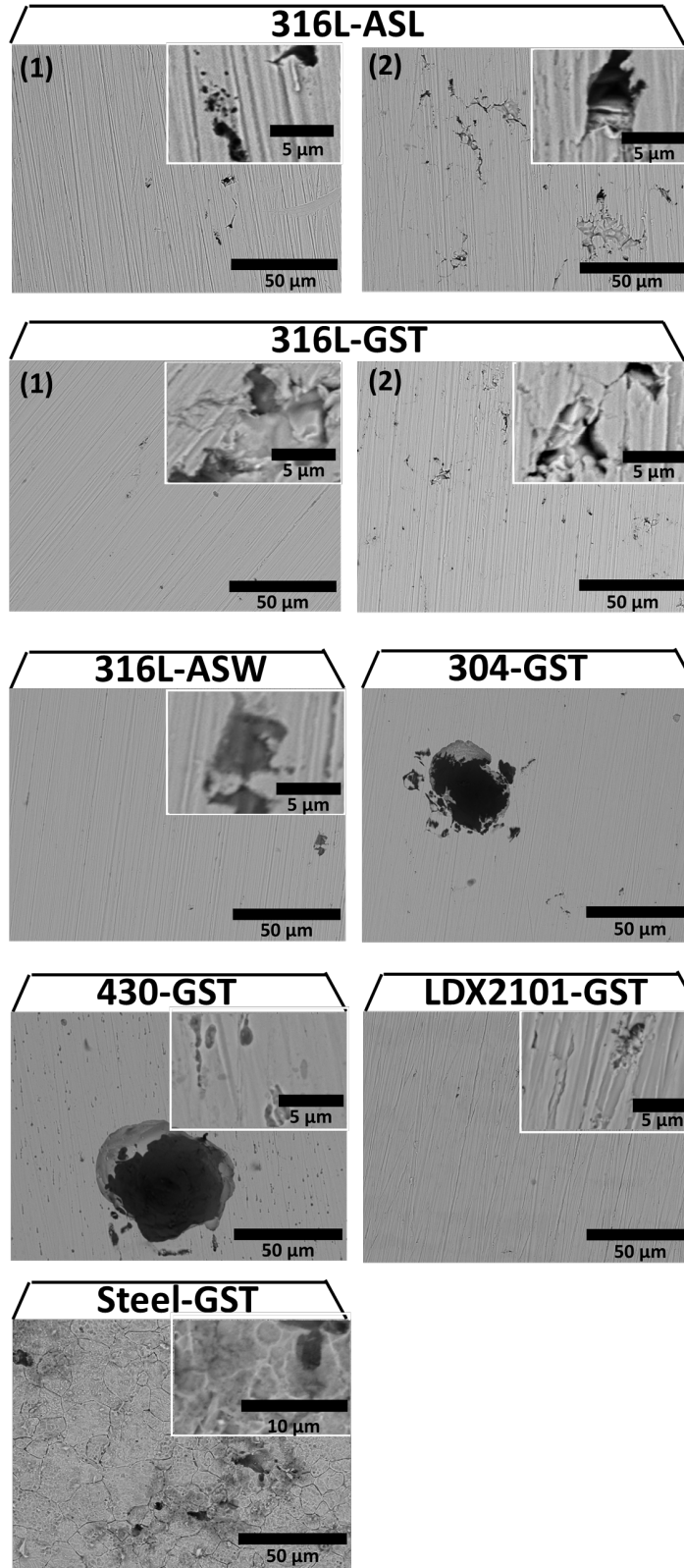


Figure S3. Post-polarization SEM images of 316L (duplicate coupons in ASL and GST, one coupon in ASW), and 304, 430, LDX2101 and low-alloyed steel (all in GST) with the same magnification. The inset in the upper right images shows a higher magnification.

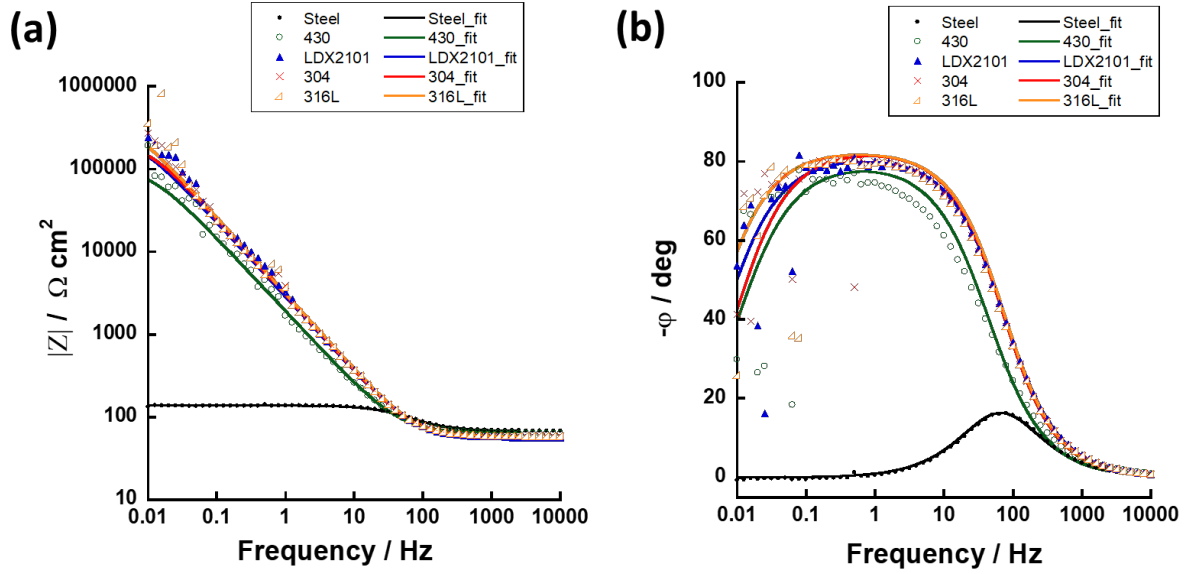


Figure S4. Bode plots of impedance modulus (a) and negative phase angles (b) as a function of frequency for the steel, 430, LDX2101, 304, and 316L exposed in GST (pH 1.5; prior to measurement: 2 h pre-passivation followed by 1 h stabilization at OCP). The lines represent the fits and the individual points represent average data of 4-5 individual measurement data sets.

Table S2. Fitted electrochemical elements of experimental EIS spectra for investigated specimens in GST. The data were based on average values of 4-5 measurements for each grade, and the error represents the uncertainty of the fit to these average data.

Grade	$R_{ct}$ ( $k\Omega \text{ cm}^2$ )	$R_s$ ( $\Omega \text{ cm}^2$ )	n	$C_{eff}$ ( $\mu\text{F cm}^{-2}$ )	$\chi^2$ ( $\times 10^{-3}$ )
<b>430</b>	$113.44 \pm 36.79$	$64.96 \pm 1.04$	$0.89 \pm 0.0059$	$54.95 \pm 1.09$	3.86
<b>LDX2101</b>	$271.35 \pm 319.98$	$56.61 \pm 0.17$	$0.91 \pm 0.0018$	$37.23 \pm 0.30$	0.11
<b>304</b>	$221.16 \pm 69.56$	$58.78 \pm 1.06$	$0.92 \pm 0.0055$	$38.05 \pm 0.74$	4.61
<b>316L</b>	$423.51 \pm 176.06$	$58.78 \pm 1.44$	$0.92 \pm 0.0067$	$36.46 \pm 0.83$	8.62
<b>Steel</b>	$0.070 \pm 0.00013$	$68 \pm 0.061$	$0.88 \pm 0.0019$	$46.30 \pm 0.51$	0.00595

## S2.3 Bioaccessible concentrations

Table S3. Bulk composition and bioaccessible concentration of released Ni from all alloys after 4 and 168 h of exposure in ASL, ASW and GST. Data are calculated based on released amounts per surface area. Results for Ni metal are included for comparison. The bioaccessible concentration of the Ni metal equals 100% per definition, eq. (4). <LOD means below limit of detection. The limits of detection vary as a function of solution and slight differences in exposed surface areas.

Materials	Solutions	Ni bulk content (wt.%)	Bioaccessible concentration (wt.%) – 4 h of exposure	Bioaccessible concentration (wt.%) – 168 h of exposure
<b>316L</b>	ASL	10	0.0033	0.011
	ASW		0.30	0.19
	GST		0.027	0.013
<b>304</b>	ASL	9.0	0.011	0.019
	ASW		<LOD (0.52)	0.17
	GST		0.015	0.011
<b>430</b>	ASL	0.11	0.0012	0.00036
	ASW		<LOD (0.54)	0.0043
	GST		<LOD (0.0021)	0.00034
<b>LDX2101</b>	ASL	1.6	<LOD (0.0081)	<LOD (0.0071)
	ASW		<LOD (0.34)	0.0066
	GST		<LOD (0.002)	0.0017
<b>Low-alloyed steel</b>	ASL	0.034	<LOD (0.0076)	0.13
	ASW		1.10	0.54
	GST		0.030	0.035
<b>Ni</b>	ASL	99.995	100	
	ASW			
	GST			

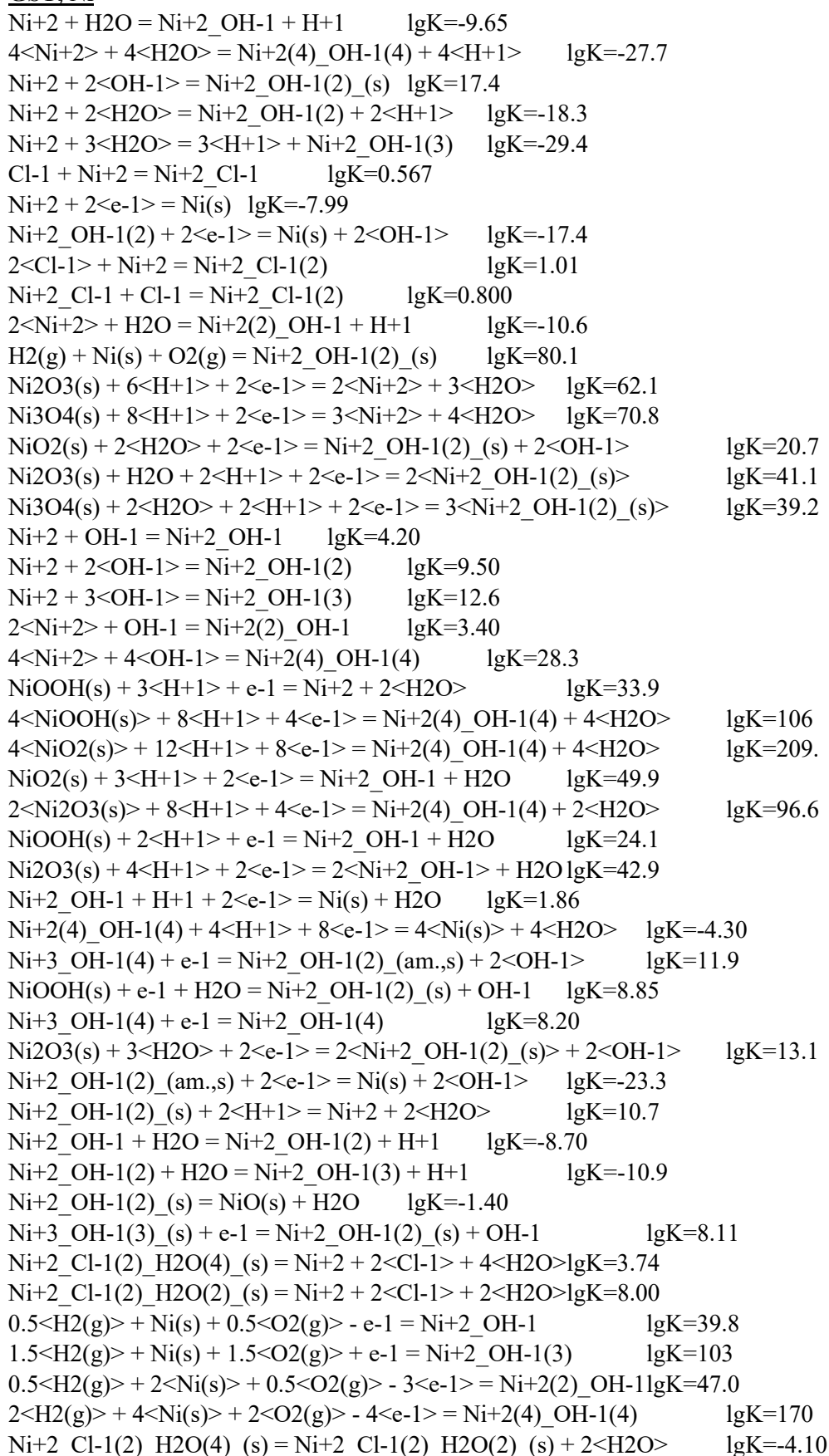
Table S4. Bulk composition and bioaccessible concentration of released Co from all alloys after 4 and 168 h of exposure to ASL, ASW and GST. Data is calculated based on released amounts per surface area. Results for Co metal are included for comparison. The bioaccessible concentration of the Co metal equals 100% per definition, eq. (4). <LOD means below limit of detection. The limits of detection vary as a function of solution and slight differences in exposed surface areas.

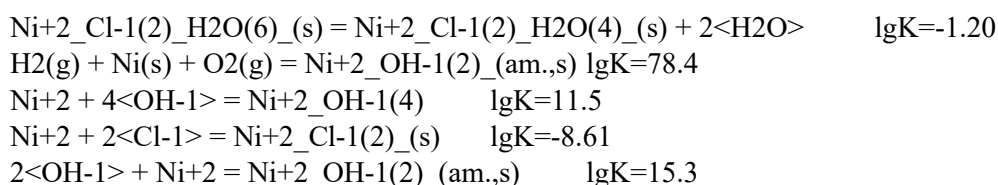
Material	Solution	Co bulk content (wt.%)	Bioaccessible concentration (wt.%) – 4 h of exposure	Bioaccessible concentration (wt.%) – 168 h of exposure
316L	ASL	0.24	0.00071	0.021
	ASW		0.00034	0.00064
	GST		0.00037	0.00042
304	ASL	0.16	0.0082	0.11
	ASW		<LOD (0.0067)	0.00016
	GST		0.00041	0.00041
430	ASL	0.019	0.0018	0.0033
	ASW		<LOD (0.0071)	0.000061
	GST		0.00010	0.00047
LDX2101	ASL	0.039	0.0011	0.011
	ASW		0.00087	0.00016
	GST		<LOD (0.00046)	<LOD (0.00011)
Low-alloyed steel	ASL	0.015	<LOD (0.0076)	0.88
	ASW		0.022	0.017
	GST		0.044	0.022
Co	ASL	99.9	100	
	ASW			
	GST			



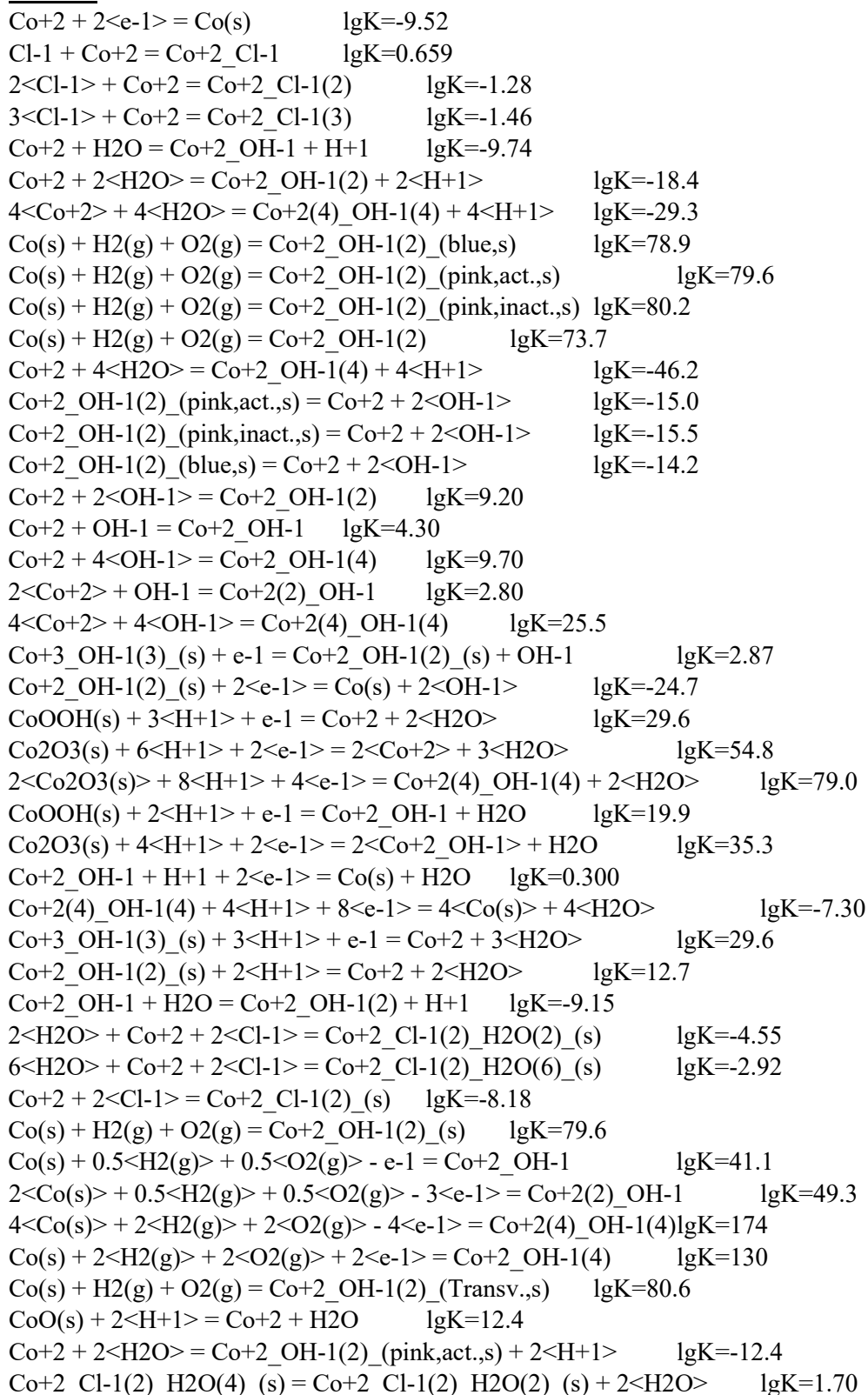
## S2.4 Included reactions in JESS chemical speciation modelling

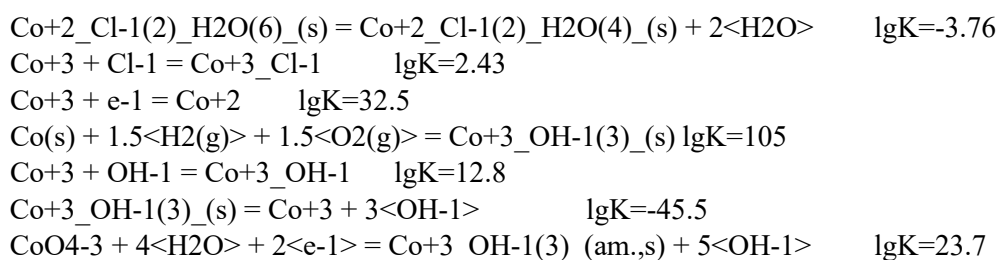
### GST, Ni



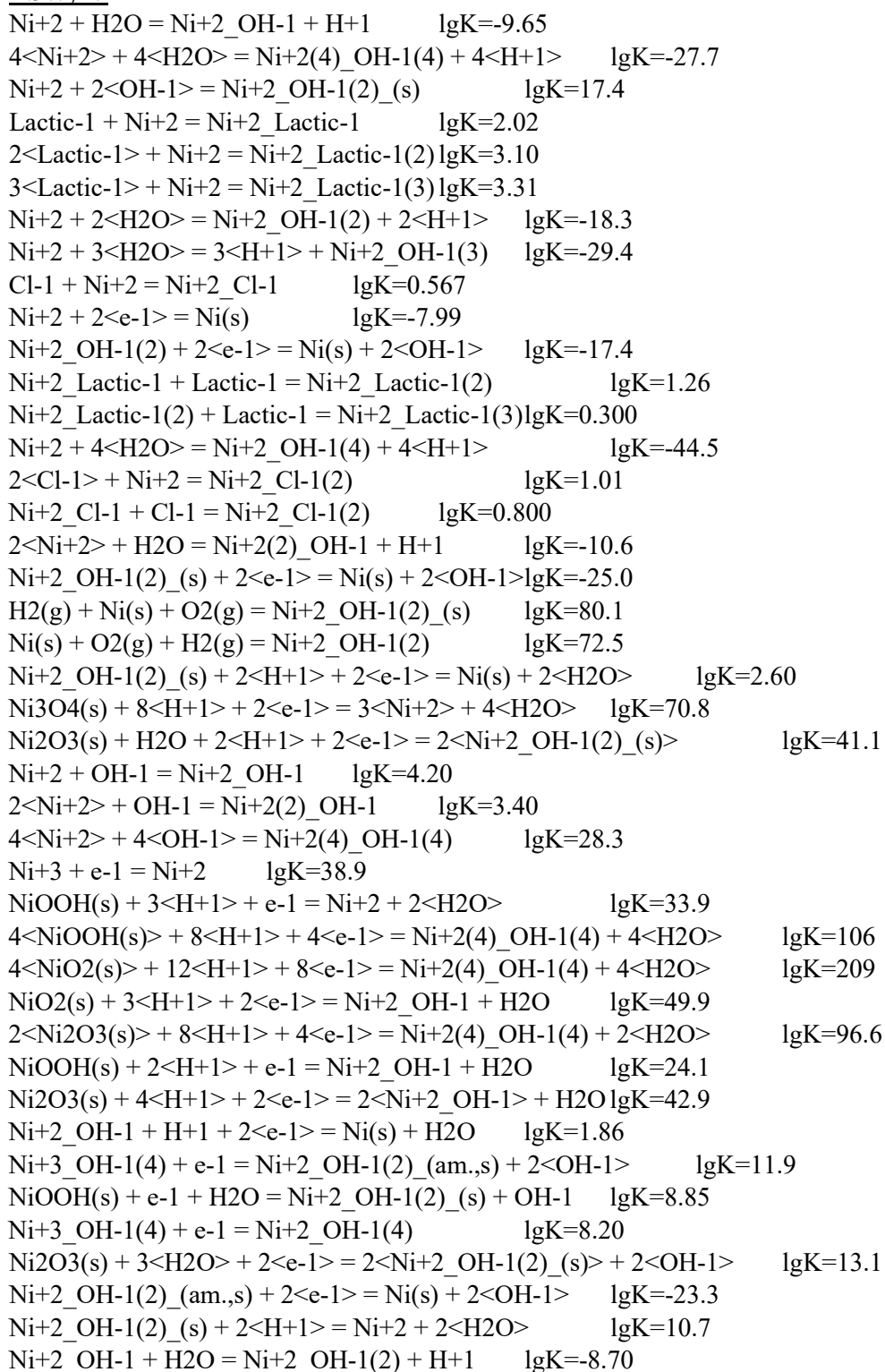


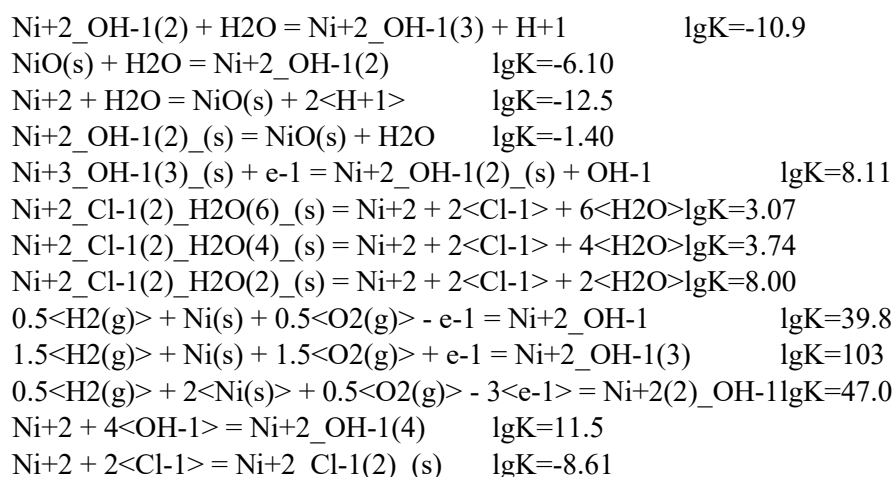
### GST Co



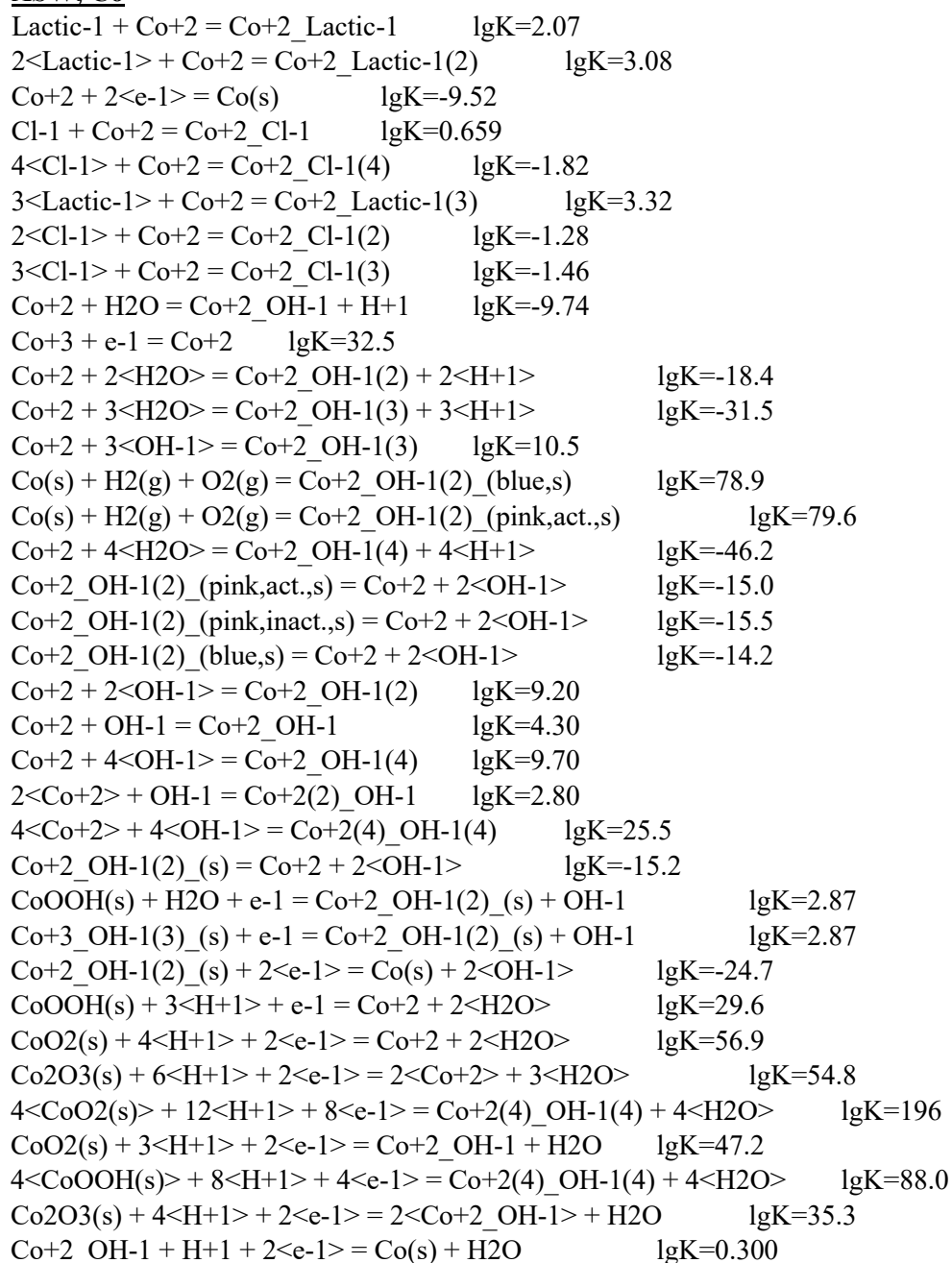


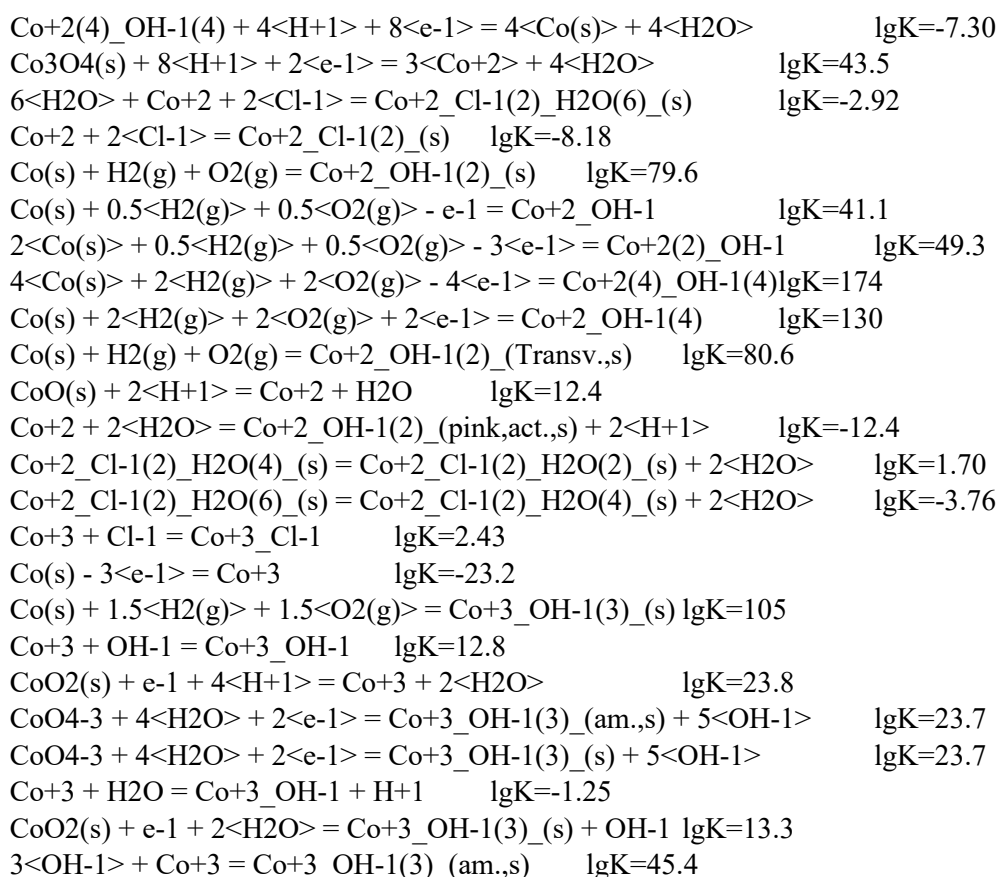
### ASW, Ni



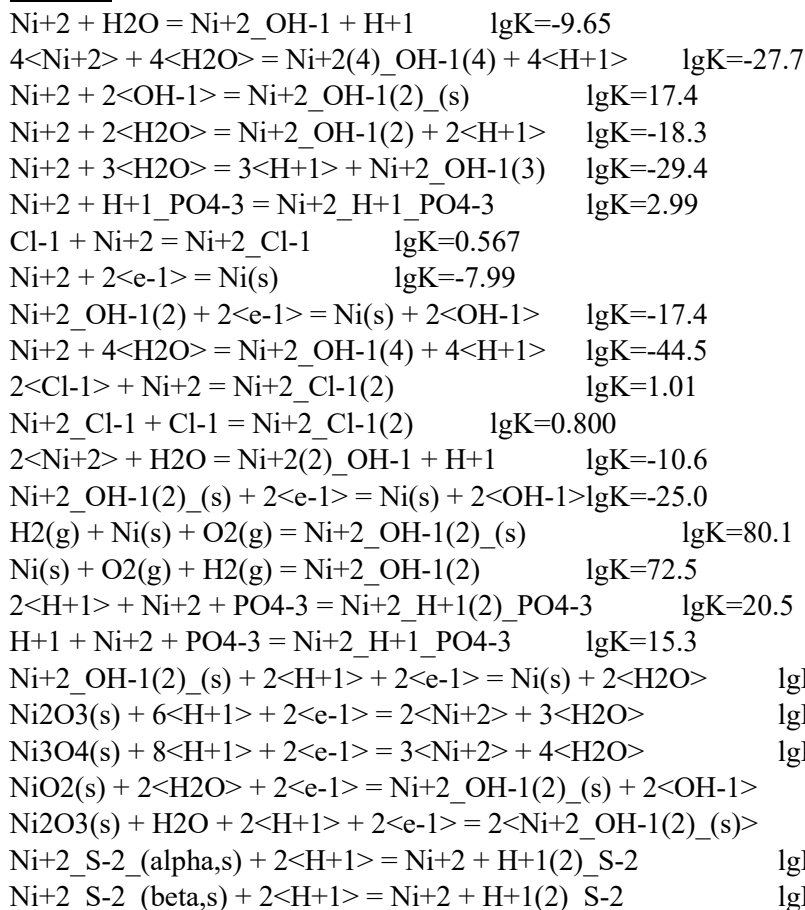


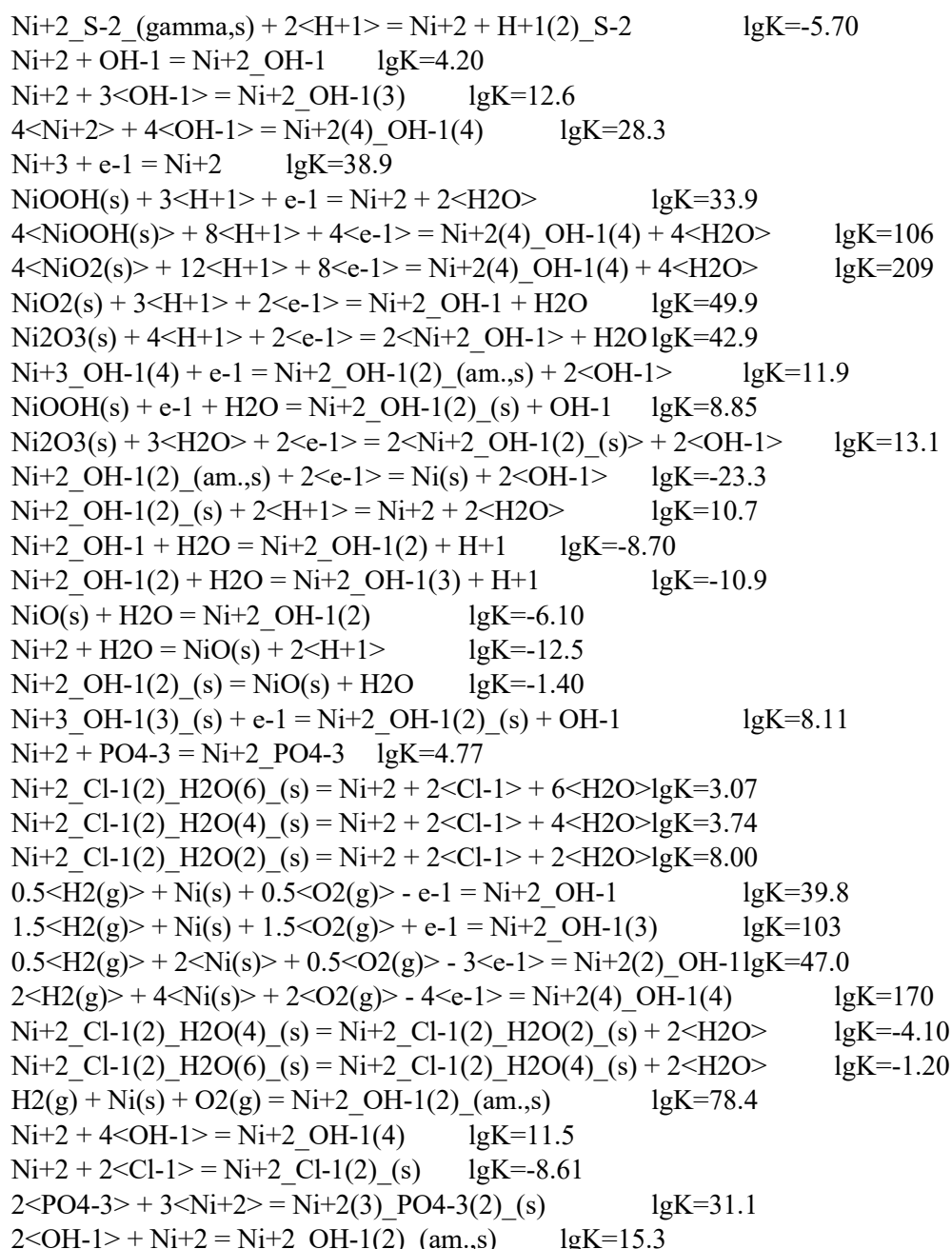
### ASW, Co



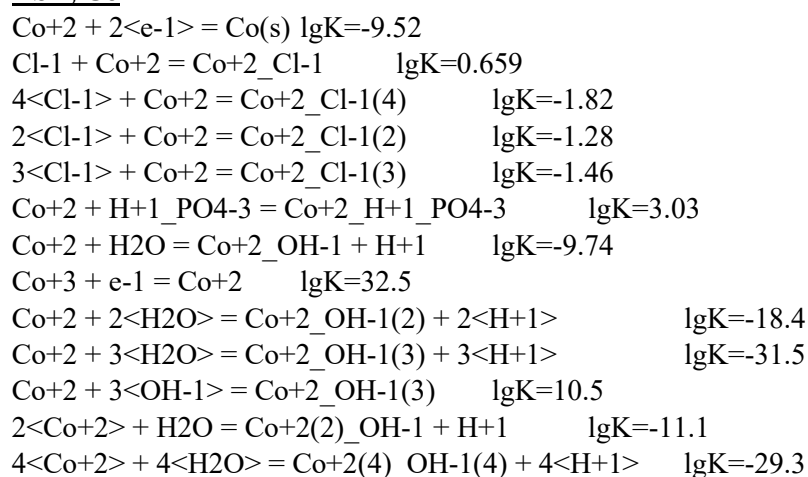


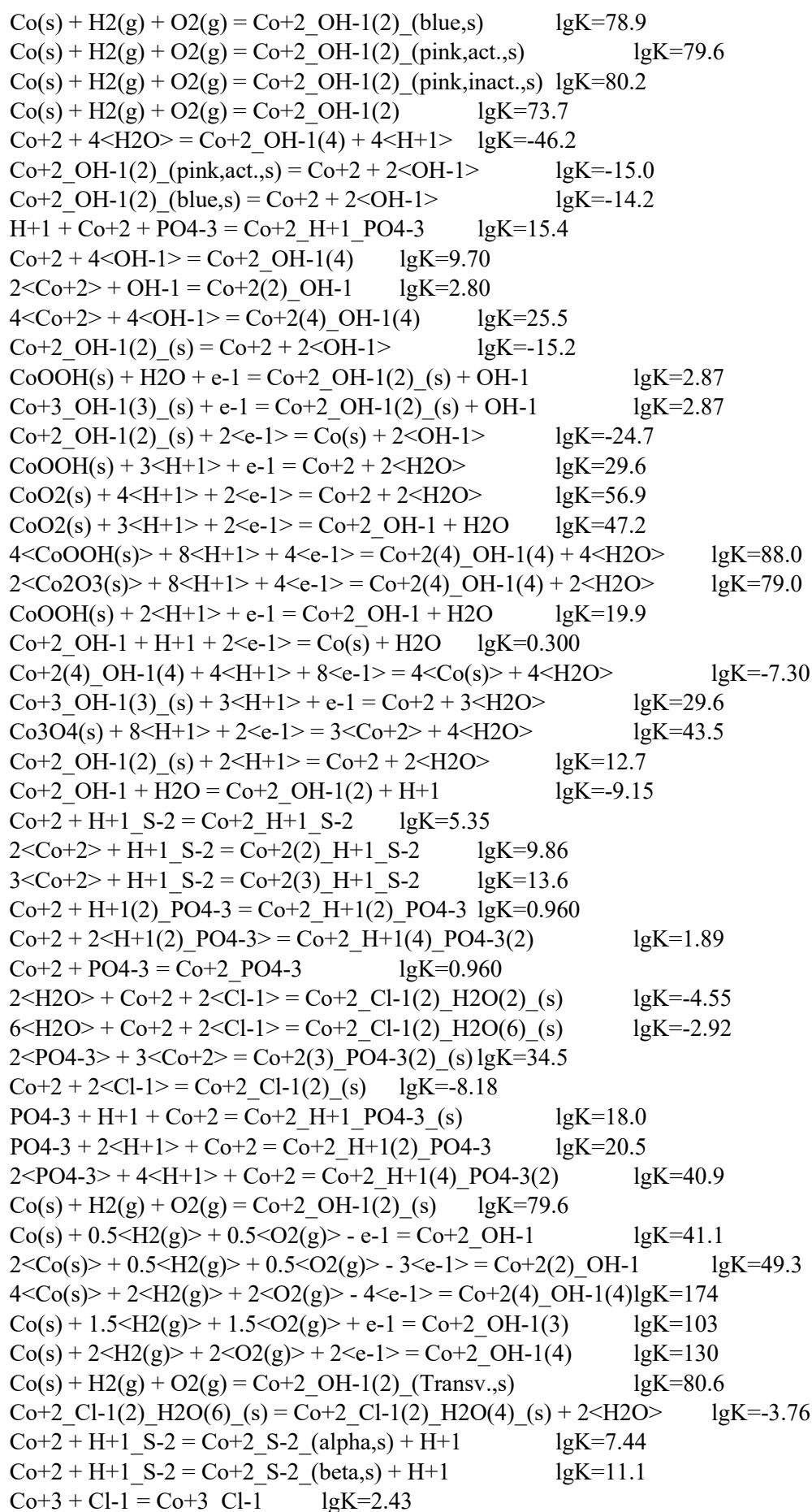
### ASL, Ni

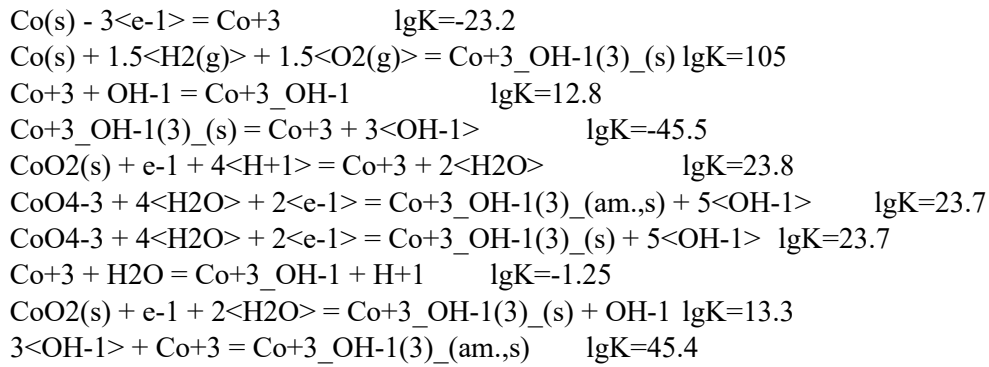




### ASL, Co







## References

- [1] P. Córdoba-Torres, T.J. Mesquita, O. Devos, B. Tribollet, V. Roche, R.P. Nogueira, On the intrinsic coupling between constant-phase element parameters  $\alpha$  and  $Q$  in electrochemical impedance spectroscopy. *Electrochim. Acta.* (72) 2012 172-178.
- [1] G J Brug, A L G Van Den Eeden, M Sluyters-Rehbach, J H Sluyters, The analysis of electrode impedances complicated by the presence of a constant phase element, *J. Electroanal. Chem.* 176(1-2) (1984) 275-295.