CHAPTER 10.17

Electrorefining

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Electrorefining is the purification of metal by the simultaneous electrolytic dissolution of impure metal and the electrodeposition of the same metal at a higher purity level. Electrorefining is often critical to meeting final purity specifications for metals such as copper, gold, lead, and silver that are smelted or made into a moderately pure precursor material. Electrorefining is also important to many industries, such as the electronics industry, that rely on high-purity metals.

The general background information that is discussed in Chapter 10.16, "Electrowinning," also applies to electrorefining. However, there are several key differences between electrowinning and electrorefining. The most important difference is that in electrorefining the anode consists of the metal that is to be refined. Correspondingly, the reaction at the anode is primarily metal dissolution in electrorefining instead of water oxidation, which generates bubbles and acid mist, at relatively inert anodes in electrowinning. Another key difference is the much lower energy requirement and higher current efficiency for electrorefining than for electrowinning. The use of anodes with inclusions that can become suspended particles is another important aspect of electrorefining that is not present in electrowinning.

Figure 1 shows the relationship between electrochemical potential and the logarithm of the absolute value of the current density for an electrorefining scenario. The applied potential or voltage for electrorefining is as much as one order of magnitude lower than that for electrowinning. Thus, the corresponding energy requirement for electrorefining is much lower than for electrowinning. The main difference is the absence of a cell voltage difference between the anode and cathode half-cell reactions. The other difference is the absence of a relatively large overvoltage needed to drive the water oxidation reaction that is often utilized for electrowinning but not electrorefining.

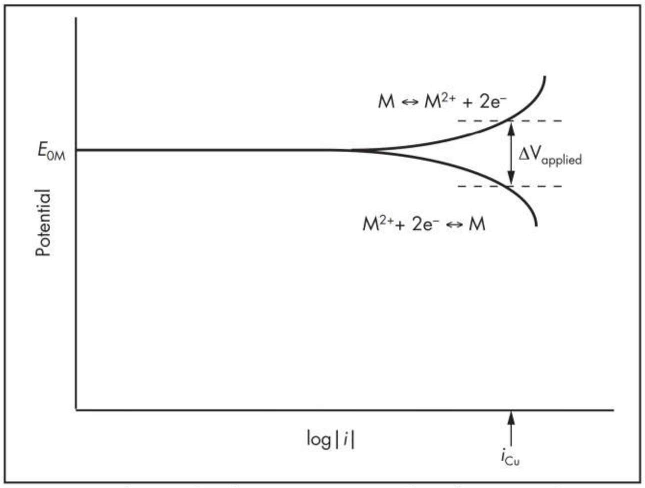

Figure 1 Relationship between potential and current density for an electrorefining cell

The anodes used in electrorefining contain impurities that are distributed between the atoms of the main metal as interstitial impurity atoms based on their solubility in the metal when the metal solidifies. Impurity atoms that are present at levels higher than their solubility limit in the main metal are also found in separate crystals of a wide variety of secondary or tertiary phase compounds. Consequently, examination of anode cross-sections using scanning electron microscopy reveals a variety of inclusions that are made up of the impurity-bearing compounds as illustrated in Figures 2 and 3.

Anode inclusions are typically only a few micrometers in diameter. As the surrounding matrix of the main metal is electrochemically forced to dissolve during the electrorefining process, these inclusions are dissolved in the electrolyte, released into solution, or form a layer of particles that often adheres to the anode. The released particles are referred to as *slimes* because they form a fine sludge of fine particles that is often "slimy." The layer of adhering slimes is often referred to as a *slimes layer*. Because the slimes consist of microscopic particles, a significant portion of slimes remaining in suspension become available to be transported to and incorporated in the cathode as impurity particles unless they are retained inside of anode bags, remain in the slimes layer, or settle to

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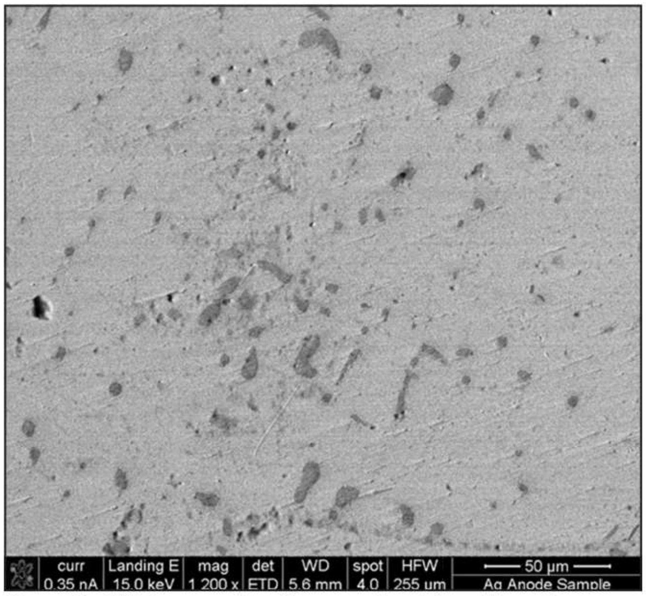

Figure 2 SEM image of a silver anode with gold- and copper-based inclusions

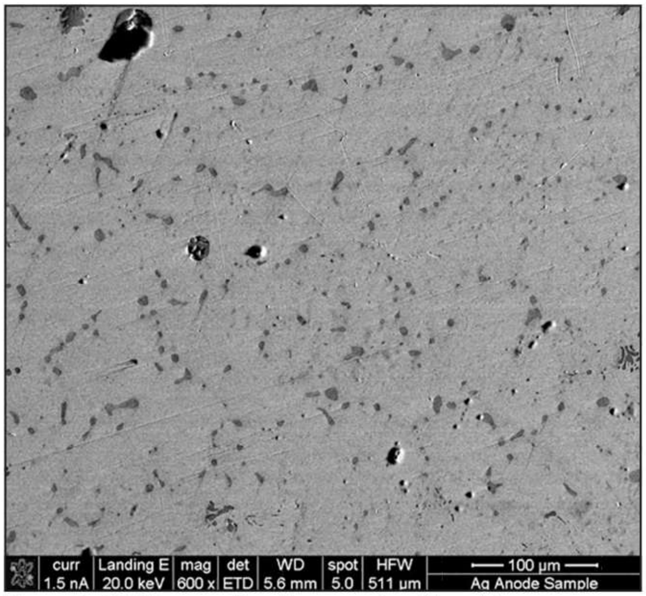

Figure 3 SEM image of a silver anode with gold-, copper-, and selenium-based inclusions

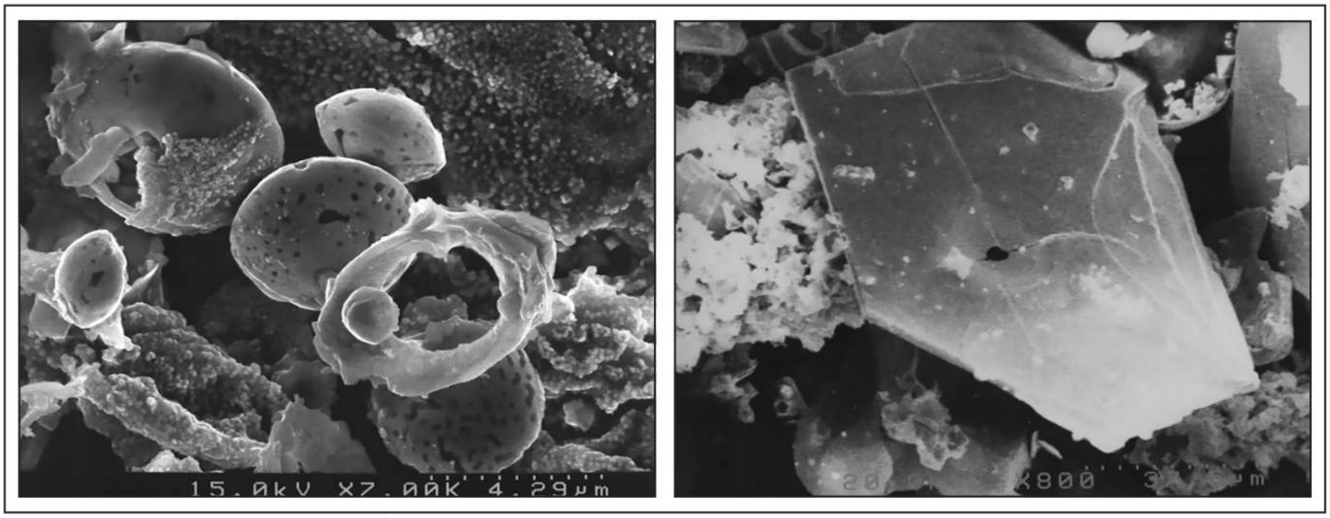

Figure 4 SEM images of copper anode slimes

the bottom of the cell. SEM images of slimes generated during the dissolution of commercial copper anode are shown in Figure 4. These images reveal the presence of cuprous selenide (Cu_2Se) rings and spheres, a kupferglimmer platelet, lead sulfate ($PbSO_4$) crystals, and silver crystallites.

In copper and lead electrorefining, anode bags are not normally used. In silver and nickel refining, anode bags are commonly used. In most cases, a significant portion of the slimes particles that are generated either fall to the bottom of the cell (or anode bag) where they are periodically collected or remain in adherent slimes layers attached to the anode. However, residual suspended slimes particles are often a major source of cathode contamination.

COMMERCIAL PRACTICE

The electrorefining of high-purity metals has been practiced commercially for cobalt, copper, gold, indium, lead, nickel, silver, and tin. Copper is the largest tonnage metal that is electrorefined. As such, industrial aspects of copper electrorefining will be discussed in detail. Lead, nickel, silver, and gold will also be discussed in this chapter.

Copper

Most of the world's refined copper is produced by electrorefining. The source material for electrorefineries is both primary ore and recycled scrap. Following pyrometallurgical processing, fire-refined blister copper is cast into anodes, which are fed into the electrorefinery. These anodes are electrolytically dissolved into a solution of primarily copper sulfate and sulfuric acid. Simultaneously with anode dissolution, copper is electrodeposited at the cathode. Cathodes are harvested and either sent to market or to a downstream processing facility.

Copper electrorefining operating data has been collected periodically and reported every three to four years at international copper conferences since 1987. Detailed operating data from seven refineries collected in 2013 are presented in Table 1 (Moats et al. 2013).

Most anodes are cast in molds on rotating wheels or discs at the smelter. Improved control of anode weight and dimensions has occurred over the years through automation. Anodes once received at the refinery are almost always prepared by a machine that presses the anodes flat, turns the ears slightly to improve their ability to hang straight in the cell, and mills the contact surface where the ears will touch the intercell contact bar.

Anodes are usually placed in an empty cell following draining, removal of slimes, and cleaning. Some newer facilities place anodes using automated cranes, while older plants use manual cranes. Most tankhouses now employ polymer concrete for the cell material while older facilities use lined concrete. After the anodes are placed, cathodes are inserted between the anodes, although in some facilities, cathodes and anodes are inserted together. Finally, the electrolyte is returned to the cell. Once the cell (or section of cells) reaches a specific temperature (varies by operation), the cell is electrified and electrorefining commences.

An anode cycle is typically 21–28 days depending on the thickness of the anode and the current density employed. Each anode cycle produces two or three crops of cathodes. Some residual anode material is removed from the cell at the end of the electrorefining cycle to avoid parts of the anode breaking free and falling to the bottom of the cell. In 2013, the average amount of the residual anode material that was removed as scrap after the process was completed was 13.7% (Moats et al. 2013). The changing of cathodes and anodes, as well as the cleaning of the cells, contributes to downtime and less than 100% time efficiency.

Anode composition can affect the performance of the electrorefinery. The average anode composition from the 2013 survey is presented in Table 2. During dissolution, more noble elements (Au, Ag), compounds that dissolve slowly or are insoluble (Cu_2Se, nickel oxide [NiO], cassiterite [SnO_2]), and compounds that form by precipitation (antimony arsenate [$SbAsO_4$], $PbSO_4$) form a slimes layer on the anode. These slimes are valuable because of their gold and silver content, but they are also a source of possible contamination of the cathode. They are collected when the anodes are removed from the cell and sent to a separate facility for processing.

Soluble elements that are less noble than copper (Ni, As, Sb, Bi) and compounds that dissolve easily (cuprous oxide [Cu_2O]) report to the electrolyte. Dissolution of other elements and Cu_2O increases copper and impurity levels that are not balanced by the cathode deposition. This requires a continual bleed of electrolyte to remove excess copper from solution and other impurities such as Ni, As, Sb, and Bi. Copper is liberated or removed from the bleed stream by electrowinning in a process referred to as *liberation*. Liberation is typically conducted in stages to decrease the copper content of the electrolyte bleed stream. In the last stage when copper concentrations are low, As, Sb, and Bi are co-deposited. The contaminated product from the last liberation stage is returned to a smelter for reprocessing. During the last stage of liberation, the production of arsine gas is possible, which requires monitoring and the use of either hooded cells or cells placed outside. Ni is recovered at several plants by evaporation or precipitation after liberation. Black acid (solution after liberation) or acid recovered by ion exchange is returned to the electrorefinery as makeup acid.

Arsenic, antimony, and bismuth are considered problem elements from a hygiene (As) or contamination (Sb, Bi) perspective. The problems related to antimony and bismuth are mitigated if the anodes contain an As/(Sb + Bi) molar ratio ≥ 2 (Krusmark et al. 1995; Noguchi et al. 1995; Wesstrom 2014). Maintaining the proper ratio is believed to mitigate the problems associated with Sb and Bi by promoting the precipitation of $SbAsO_4$ and bismuth arsenate ($BiAsO_4$) in the slimes layer. Improper anode chemistry can lead to floating slimes, pipe scaling, and anode passivation (Wesstrom 2014). If antimony concentration becomes too high in the electrolyte, it will lead to the formation of colloidal particles that can float on the electrolyte surface. These *floating slimes* often become incorporated in the cathode, leading to nodulation and contamination near the top of the cathode. These nodules become a source of short circuits, which lower current efficiency. High antimony levels can also lead to scale formation on cell walls and pipes, which can cause flow issues within a plant.

Anode passivation is another potential problem. It is caused by trying to dissolve the anode too fast relative the chemistry of the anode, electrolyte composition, and temperature. Anode passivation leads to uneven anode dissolution and/or poor cathode deposits. Anode passivation can be alleviated by operating at lower current density, higher temperature, higher chloride concentration, or higher arsenic concentrations in the anode (Moats and Hiskey 2010).

Cathodes are deposited for 7–14 days. Newer facilities use stainless-steel sheets that are often referred to as *mother blanks*, whereas older plants use very thin *starter* sheets of copper as the cathodes on which the electrorefined copper is deposited. Starter sheet cathode tankhouses usually plate at lower current density (on average at 278 A/m^2) for longer times (10–14 days) at lower current efficiency (95.5%) than stainless-steel cathode facilities (312 A/m^2, 5–7 days, 96.6%; Moats et al. 2013). For these economic reasons, many electrorefineries have upgraded to stainless-steel cathodes over the past two decades.

The high-purity (>99.99%) copper that deposits on the cathode sheets is usually smooth and dense in plate or sheet form with enough ductility to be harvested by automated mechanical stripping. To achieve this, electrolysis parameters are well controlled. These parameters include current density, temperature, electrolyte composition, electrolyte flow, and the use of additives. Average current density at copper electrorefineries in the 2013 survey was 310 A/m^2 (Moats et al. 2013). This value has been increasing over the past two decades. Some electrorefineries operate at 400 A/m^2 with the use of parallel electrolyte flow (Mettop-BRX technology). Electrolyte temperature and composition are monitored and controlled through the use of heat-retention blankets or cell covers, heat exchangers, and electrolyte bleeding. Copper electrolyte refineries typically operate near 65°C with an average electrolyte composition of 49 g/L Cu, 173 g/L H_2SO_4 (sulfuric acid), 5.5 g/L As, 0.3 g/L Sb, 0.2 g/L Bi, and 13.0 g/L Ni. Glue, thiourea, chloride, and occasionally Avitone A (a sodium alkyl sulfonate) are used as additives to control the surface morphology and crystal structure.

In electrorefining, the flow of electrolyte is maintained to ensure even flows to each cell, to provide additives at the correct concentrations, and to ensure that there is no turbulent flow, which would otherwise increase oxygen dissolution from the air and reduce current efficiency because of the reduction of oxygen at the anodes.

Table 1 Operating data from seven copper electrorefineries

	Refinery						
	Brixlegg, Austria	**Las Ventanas, Chile**	**Hamburg, Germany**	**Naoshima, Japan**	**Onsan Refinery 1, Korea**	**Magna, UT, USA**	**El Paso, TX, USA**
Nameplate cathode capacity, t/a	120,000	400,000	416,000	234,000	360,000	281,000	455,000
2012 production, t	113,600	398,000	365,706	213,996	352,192	190,000	195,080
Anodes							
Analysis	Typical	(4 brands)					
Cu, %	>99.2	99.5–99.7	98.5–99.6	99.2	99.5	99	98.9–99.7
Ag, ppm	400	190–450	200–2,000	856	772	462	160–1,200
Au, ppm	6	1–20	10–150	40.5	50.2	52	1 -15
S, ppm	8	10–40	10–70	30	10	38	7–30
Se, ppm	<10	110–220	200–600	480	404	784	200–1,000
Te, ppm	<10	1–10	20–200	180	146	118	10–100
As, ppm	100	500–900	400–1,500	1,330	1,456	1,113	30–200
Sb, ppm	200	20–300	100–600	220	229	46	30–400
Bi, ppm	30	5–20	20–250	380	250	679	5–100
Pb, ppm	2,000	10–300	200–2,000	2,340	195	2,121	10–600
Fe, ppm	25	10–40		10	Not analyzed	13	5–100
Ni, ppm	3,000	80–400	1,000–5,000	1,940	758	271	50–600
O, ppm	1,000	1,400–2,000	1,000–2,000	1,160	1,223	1,709	1,050–2,400
Conventionally or continuously cast	Conventional	Conventional	Mold on wheel	Conventional	Mold on wheel	Conventional	Mold on wheel
Automatic weight control	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Anode preparation machine	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Weighing	Yes	Yes	Yes	No	No	Yes	Yes
Straightening	Yes	Yes	Yes	Yes	Pressed	Yes	Yes
Lug milling	Yes	Yes	Yes	No	Yes	Yes	Yes
L × W × T, mm	990 × 945 × 38/45	915 × 895 × 39	950 × 905 × 55	980 × 960 × 44	1,183 × 1,170 × 50	1,038 × 938 × 39	940 × 921 × 51
Mass, kg	292/350	276–280	397	373	415	335	388.2
Life, days	14	16	21	23	21	20	28
Scrap, %	13.5	18–19	10–12	14	11	18	13
Anode Slimes							
kg/t of anode	5	1.9	5–8	6.4	2.6	9.7	2–4
Removed after no. days	14	16	21	23	21	20	28
Anode slimes analysis, %							Autoclaved assays
Cu	<1 (after leach)	25–27	12–19	12.3	18.9	30	1
Ag	4–8	140–180	10–20	8.1	13.3	5	20
Au	0.05–0.1	3–4	0.4–1.0	0.58	0.79	0.5	0.2
S		5–6				0	12
Se	0.1–0.2	8–9	4–8	4.24	13.6	5	20
Te		0.5–2	1–2	1.83	2.2	1	0.4
As	0.5–1.0	5–6	2–3	2.83	2.9	5	2
Sb	1.0–5.0	4–5	3–5	1.31	0.6	1	4

(continues)

Table 1 Operating data from seven copper electrorefineries (continued)

	Refinery						
	Brixlegg, Austria	**Las Ventanas, Chile**	**Hamburg, Germany**	**Naoshima, Japan**	**Onsan Refinery 1, Korea**	**Magna, UT, USA**	**El Paso, TX, USA**
Bi		0.2–0.3	1–2	2.51	0.9	3	0.7
Pb	25–40	5–6	11–18	21.23	14.5	30	5
Fe		0.1–0.2				0.25	0.04
Ni	1.0–4.0	0.5–1	1–4	1.23		0.05	0.05
Other					13.1% Ba		
Electrolytic Cells							
Commercial cells	312	1,880	1,080	808	1,140	1,400	2,504
Stripper cells		126		88	0	0	216
Liberator cells	15	32	3–8	36	276	24	5 plus 16 at nickel plant
Cell construction	KVK polymer concrete	Polymer concrete	Polymer concrete	Reinforced concrete	Polymer concrete	Polymer concrete	CTI polymer concrete
Lining material		No		Semiflexible PVC	None	None	N/A
L × W × D, mm	5,900 × 1,180 × (1,370–1,560)	4,101 × 1,080 × 1,280	6,350 × 1,171 × (1,330–1,500)	5,400 × 1,200 × (1,250–1,400)	4,970 × 1,066 × (1,460–1,317)	4,812 × 1,194 × 1,524	4,456 × 1,099 × 1,194
Anodes/cathodes per cell	57/56	40/39	63/64	54/53	50/49	47/46	38/39
Anode spacing, center to center, mm	100	100	95	97	98	98	102
Electrode spacing, anode face to cathode face, mm							
Crop 1	28/26	28	19	26	20	28	25.5
Crop 2	35/31		27	35	30	40	14.75
Crop 3	–/35	–	35		40		N/A
Busbar area, A/mm^2	1.0	–		1.18		0.55	0.72
Cell Inspection							
Times/day	14 h/d	2	15	1	3~9	1	1
Infrared camera, handheld, or crane	Yes, handheld	Handheld	Handheld camera	Handheld	Handheld	Handheld	Handheld
Infrared gun	No	Check	No	No	No	No	Training
Cell voltage monitoring	Yes	Section voltage	Yes	No	Yes	No	Every 4 h on section
Gauss meter	Yes	Yes	Yes	No	Yes	Yes	Yes
Electrical							
Amperage per cell	38,000/44,800	21,600–22,000		27,500	30,900	25,500	17,500–18,000
Cathode current density, A/m^2	340/400	310	335	260	316 (Design 325)	285	255–271
Cell voltage, mV	300–400	300–450	330	330	340	280	
AC/DC converting equipment	Thyristor	Siemens rectifier	3 Si rectifiers	2 Thyristor rectifiers	4 Rectifiers	4 Thyristor rectifiers	SCR rectifier
Converter capacity, kA and V	38 kA,140 V/ 50 kA, 100 V		40 kA, 160–180 V	33 kA/183 V	35 kA (200 V, 150 V, 100 V, 30 V)	27,600 kW; 269 & 360 V	6,000 kW, 325 V DC
Cathode current efficiency, %	95–99	93–94	93–97	97.5	98.3	94.7	97
Rectifier output energy, kW·h/t of cathode		360		280	329	340	290
Periodic reverse current?	Yes	No	No	No	No	No	No

(continues)

Table 1 Operating data from seven copper electrorefineries (continued)

	Refinery						
	Brixlegg, Austria	**Las Ventanas, Chile**	**Hamburg, Germany**	**Naoshima, Japan**	**Onsan Refinery 1, Korea**	**Magna, UT, USA**	**El Paso, TX, USA**
Section switches and type	Hundt & Weber	Manually operated	Hundt & Weber	Pneumatic	Pneumatic	Yes, air brake	No
Time efficiency, %	98.5	95–96	96.8	98	98.2	91	96
Electrolyte							
Cu, g/L	45–50	46–52	45–49	51.4	45~47	45	40–50
Free H_2SO_4, g/L	160–180	165–185	170–200	182	170~175	170	170–200
As, g/L	0.2–0.3	8–10		7	6.1	12.8	9 -10
Sb, g/L	0.4–0.5	0.50–0.6		0.3	0.28	0.06	0.3–0.55
Bi, g/L	0.01	0.01–0.03		0.3	0.36	0.04	0.05–0.08
Ni, g/L	18–22	2.5–3.3		20.7	14.7	4.3	13–16
Fe, g/L	0.1–0.2	0.6–1.0			0.42	0.4	1.1
Cl, g/L	0.04	0.04–0.05		68	0.04	0.04	0.02–0.06
Cell inlet temperature, °C	65		63	67	65	65	65.5
Cell outlet temperature, °C	65	64–66	63	66	63	62	63–65.5
Circulation, L/min/cell	25–75	62–64		35	25	20	20–26.5
Distribution system	Conventional, Mettop-BRX	18–20	No	Manifold	Manifold (bottom-in, top-out)		Head tank manifold
Filtered	Yes	10%–20%	No	Ultrafilter	Scheibler	Yes, 15% of total volume	Slimes return only
Circulating pumps	Centrifugal	Centrifugal	Horizontal centrifugal	Vertical	Vertical	Horizontal centrifugal	Horizontal centrifugal
Purification method	Liberator cells, nickel sulfate plant	Bleed to hydrometallurgical process	Cu liberation, evaporation, electrowinning; Ni, Fe, As removal	Liberators & $NiSO_4$ by concentration	Activated carbon, decopper	Cu liberation, bleed to hydrometallurgy plant for impurity control	Liberator cells, acid purification unit, nickel carbonate, sodium sulfate
Addition Agents							
Glue, g/t of cathode	45	48		120	85	73	58
Thiourea, g/t of cathode	20	62		120	111	115	18
Avitone A, g/t of cathode	10	33		4		0	15
HCl, NaCl, g/t of cathode	HCl to 0.04 g/L	55 (NaCl)		170 (HCl)	145 (HCl)	73 as NaCl	to 0.035 gpL
Automatic sensing of glue or thiourea?	No	No	Collamat (glue)	Yes	No	Collamat	No
Cathode Description	Stainless steel	Cu starting sheet	Stainless steel	Cu starting sheet	Stainless steel	Stainless steel	Cu starting sheet
Copper Starting Sheets							
L × W × T, mm		960 × 965 × 1		1,000 × 1,000 × 1.3			953 × 953 × 0.75
Mass, kg		5.2		14			6.8
Starting blanks		Titanium		Stainless steel			Ti
Cathode pressing		No		No			Yes
After no. of hours							72–76
Permanent Stainless Steel	ISA process	—	ISA process		Kidd process	Kidd process	
Stainless steel		—			316L	316L	
L × W × T, mm	1,132 × 1,046 × 3.25	—	965 × 975 × 3.25		1,070 × 932 × 3.25	990 × 990 × 3	
Mass, kg	39	—	37		40	37	
Hanger bar	ISA, Outotec	—	Hollow rectangular				

(continues)

Table 1 Operating data from seven copper electrorefineries (continued)

	Refinery						
	Brixlegg, Austria	**Las Ventanas, Chile**	**Hamburg, Germany**	**Naoshima, Japan**	**Onsan Refinery 1, Korea**	**Magna, UT, USA**	**El Paso, TX, USA**
Hanger bar material	Stainless steel + copper	—	Stainless steel, copper	Copper with steel inside	Cu-solid bar with stainless-steel sheath	Cu	
Hanger bar, L × W × T	1,342 × 30 × 43, 1,342 × 25 × 50	—	43 × 30 × 1,311	1,330 × 30 × 30	1,170 × 38 × 25	36.5 × 25.4 × 25.4	
Blade to hanger bar joint	Weld	—	Weld	Welded	Weld	Weld	
Blade side edge strip	ABS, PE*	—	ABS	Mitsubishi Snapjaws	MPPO†	PP‡	
Cathode Analysis, ppm	Typical						
Ag	7	08–09	10–17	12	7.6	10	6–15
S	6	3.0–4.0	<5	3	8.8	<4	3
Se	0.2	0.5–0.6	<0.5	<1	0.13	0.3	<1.0
Te	0.1	<0.5	<0.5	<1	0.11	0.1	<0.1–1.4
As	0.8	0.5–0.6	<1	<1	0.39	0.5	<0.1–1.9
Sb	0.5	0.5–0.7	<1	<1	0.1	0.2	<1.0
Bi	0.6	0.1–0.2	<0.5	<1	0.1	0.3	0.1–0.9
Pb	1.2	0.5–0.6	<1	<1	0.11	1.5	<0.5
Fe	0.1	0.5–1.0		<1	0.36	0.6	1–2
Ni	0.6	0.5–0.6	1	<1	0.1	<1	<1.0
Cathode Operations							
Plating time, days	7/4-5-5	8	6–8	11 or 12	7	10	13.5
Final Cu mass, kg	60–65/42–45, 53–56	120	40–76 per plate	170	120	65 per side	175
Productivity, tankhouse labor hours per ton of cathode			0.36	0.35	1.2	0.42	0.7
Washing method	Hot water	Tanks	Spray	Hot water spray	Hot water (75°C) spray	Aisco washing machine	Spray chamber
Stripping machine	Outokumpu Wenmec	No	Outokumpu Wenmec	Mitsubishi (starting sheet)	Yes	Aisco	
Machine features							
Mother blanks/hour	~600	—	500	650	432	500 maximum	
Washing	Yes	—	Yes	Yes	Yes	Yes	
Stripping	Yes	—	Yes	Yes	Yes	Yes	
Stacking	Yes	—	Yes	Yes	Yes	Yes	
Sampling	No	—	No	No	Yes	Yes	
Weighing	Yes	—	Yes	No	Yes	Yes	
Strapping	Yes	—	No	No	Yes	Yes	
Other		—			Vision system		

Source: Moats et al. 2013

* ABS = acrylonitrile butadiene styrene; PE = polyethylene.

† MPPO = modified polyphenylene oxide.

‡ PP = polypropylene.

Table 2 Average copper anode composition

Element	Concentration
Cu	99.3 %
Ag	750 ppm
Au	30 ppm
S	30 ppm
Se	400 ppm
Te	110 ppm
As	890 ppm
Sb	350 ppm
Bi	180 ppm
Pb	1,170 ppm
Fe	60 ppm
Ni	2,040 ppm
O	1,460 ppm

Source: Moats et al. 2013

Lead

The electrorefining of lead by the Betts' process is one of the first large-scale usages of electrometallurgy with the first refinery installed in 1902 at Trail, British Columbia, Canada. It involves refining 96%–99% Pb anodes produced by pyrometallurgical methods to produce >99.99% lead. The main advantages of the electrolytic route are (1) removal of bismuth, (2) production of high-purity lead, and (3) production with minimal lead dusts and fumes. The main disadvantages are (1) impurity removal/disposal from the residues and solution and (2) higher costs than pyrometallurgical refining (Thornton et al. 2001). A thorough description of the process is given by Gonzalez-Dominguez et al. (1991).

The Betts' process involves the electrolytic dissolution of lead from cast 200–300-kg anodes into the electrolyte. The electrolyte is typically based on fluorosilicic acid (H_2SiF_6) although a few plants use fluoroboric (HBF_4) or sulfamic (H_3NSO_3) acid. Both fluorosilicic and fluoroboric electrolyte plants require adequate ventilation because of the potential generation of toxic hydrogen fluoride fumes above the electrolyte. Sulfamic electrolyte can decompose into ammonia and sulfate, which can cause environmental issues. For these reasons, the use of a less toxic electrolyte, such as methanesulfonic acid, has been investigated (Jin and Dreisinger 2016).

Pb^{+2} is transported across the cell through the electrolyte. Pb plates onto Pb starter sheets produced by a highly automated process of rolled and embossed refined lead (15 ppm of Sb is added to improve stiffness). Cathode morphology is controlled by the proper levels of additives, temperature, and current density.

Cast anodes are made of lead bullion. Anode microstructure is critical. A *honeycomb* structure with uniform size grains surrounded by impurities is desired. As Pb electrolytically dissolves, a skeleton of slimes resembling a honeycomb remains. Nonuniformity of the lead grains leads to nonadherences of the slimes and uneven dissolution, which causes production difficulties. Anode microstructure is strongly influenced by As, Sb, Bi, and Ag. Slimes adhesion increases when Bi is greater than 0.23%. Slimes adhesion increases when eutectic-forming elements (As and Ag) are present. Water quenching significantly improves slimes adhesion. Control methods are used for cooling rates and casting techniques to produce homogeneous properties (Gonzalez-Dominguez et al. 1991).

The use of fluorosilicic electrolyte is most widely practiced. Electrolyte composition is 0.2–0.5 M $PbSiF_6$ (lead fluorosilicate) and 0.5–0.8 M H_2SiF_6 with milligrams-per-liter concentrations of Bi, Cu, As, Sb, and Sn. The electrolyte temperature is usually 40°C. Although noble elements are more electrochemically noble, they can still electrochemically dissolve to a small extent. Au, Ag, Cu, Sb, Bi, and As report to the anode slimes if the anode overpotential is controlled. The slimes are treated to recover high-value elements and dispose of low-value elements. Similar to copper electrorefining, lead anodes contain oxide inclusions. Because the oxide inclusions dissolve chemically, the apparent anode current efficiency, which is based on the electrolytic and chemical dissolution rates, is greater than 100%. This results in an increase of dissolved lead concentration in the electrolyte with time. Lead concentration is controlled by electrowinning or precipitation. The allowed concentrations of impurities depend on product specifications. Plants operate under conditions to avoid dissolution of noble impurities. Impurities are removed from the electrolyte by cementation on lead granules in a purification column or electrodeposition in a separate electrolysis circuit.

Lead electrorefining is performed with current densities of 120–230 A/m^2, which produce cell voltages of 0.3–0.6 V. Current efficiency is 90%–98%. The electrical energy consumption is 120–195 kW·h/t. Lead is deposited for 4–7 days in cells with 16–43 cathodes.

A flat smooth lead deposit is achieved by adding reagents to the electrolyte. These additives increase the cathodic overpotential, which is necessary to avoid rough and porous deposits. Glue, lignin sulfonate, and aloes are used. Glue is added at rates of ~600 g/t. Lignin sulfonate is introduced at 200–1,000 g/t. Aloes are added at the Trail operation at 170 g/t. The Trail controls their operation by measuring overpotential (Kerby and Jankola 1990). Betts' lead electrorefining operational data is reported by Gonzalez-Dominguez et al. (1991).

Nickel

High-purity nickel is produced by electrorefining at a few locations. Electrorefining is an older technology and has been mostly supplanted by hydrogen reduction or electrowinning as the preferred choices to produce commercial pure nickel. Electrorefining of nickel starts with either matte or impure nickel anodes. Impure metal anodes are used at Norilsk, Russia; Pechenga, Russia; and Jilin, China (Crundwell et al. 2011). An overview of the processes is given by Vignes (2013). Historic details of both types of electrorefining are provided by Boldt and Queneau (1967).

Typically, matte anodes are ~75% Ni, ~20% S with the rest as impurities. Anodes are loaded into woven polypropylene bags and placed in a cell. Nickel starter sheets are placed in a compartment between two adjoining anodes. The compartment is also covered with a woven cloth. A current density of ~250 A/m^2 is applied to electrolytically corrode nickel from the anodes and plate pure nickel metal on the starting sheet cathodes. After approximately 10 days, the enlarged cathodes are pulled and replaced with new starting sheets. Anodes are replaced after 16–17 days. Anode scrap and corrosion products are processed to recover high-value elements, such as Ni, Co, Cu, Ag, Au, and platinum group metals (PGMs). The solution inside the anode bag (i.e., anolyte) flows out of the cell and is purified and replenished in an electrolyte purification plant before being returned to the cathode bags as pure catholyte. The catholyte is returned to the cathode compartments in such a way that flow is always away from the cathodes into the anolyte, preventing catholyte contamination. Physically, this is indicated by a *head* of catholyte in the cathode compartments above the anolyte. The reader is referred to Boldt and Queneau's (1967) seminal work, *The Winning of Nickel*, for more details regarding the electrorefining of matte anodes.

Crude nickel anodes are made by casting after pyrometallurgical reduction of nickel oxide. Electrorefining occurs similarly as with nickel matte anodes. Typically, cobalt, copper, iron, lead, zinc, and arsenic chemically and/or electrochemically dissolve and report to the anolyte. These are removed during anolyte treatment prior to the return of the solution to the catholyte compartment. Silver, gold, and PGMs remain as solids and collect in the slimes, which are processed to recover these high-value elements.

Silver

The purpose of silver electrorefining is to (1) produce >99.9% silver from an impure silver material and (2) collect all of the gold and PGMs in the anode slimes for further processing and eventual recovery. Pyrometallurgical methods typically produce doré with 98%–99.5% silver. The doré is cast into small anodes, placed into anode bags, and then electrolyzed in either a Moebius cell or Balbach-Thum cell. The silver dissolves into a silver nitrate–sodium nitrate–nitric acid electrolyte. The electrolyte will contain ~150 g/L Ag with a pH of 1.0–1.5 at a temperature of ~35°C. The bags facilitate the collection of the high-value slimes. Copper, lead, and palladium will accumulate in the electrolyte. The electrolyte is treated once the concentrations of these elements reach 10 g/L Cu, 10 g/L Pb, or 1 g/L Pd. The electrolyte is processed to recover the silver and then disposed (Habashi 1998).

Because of its high exchange current density, electrodeposition of silver produces needles. These needles are periodically broken either manually or automatically to avoid short-circuiting the cell. The cells are designed to allow the breaking of the needles. Moebius cells are more commonly used now because they utilize less floor space and are easier to mechanize. Schematic diagrams for Moebius and Balbach-Thum cells can be found elsewhere (Habashi 1998; Pletcher and Walsh 1990). After removing the needles from the cell, they are washed and melted to produce silver bullion bars.

Gold

Most gold bullion is pyrometallurgically refined using the Miller chlorination process to produce 99.6% purity. For high-purity gold (99.99%) needed for coinage, electrolytic refining is required. Electrorefining of gold using the Wohlwill process removes trace amounts of silver, copper, zinc, and PGMs. Partially refined gold bullion anodes are electrolytically corroded into 60°C, 80–100 g/L Au, 80–100 g/L HCl electrolyte by the application of a current density of ~800 A/m^2. Impurities accumulate in the electrolyte or as anode sludge. The electrolyte is bled and treated to recover the gold. The sludge is recycled back into pyrometallurgical refining. Gold deposits at the cathode. The cathodes are washed with a hot sodium thiosulfate solution to remove entrained impurities (Marsden and House 2006).

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