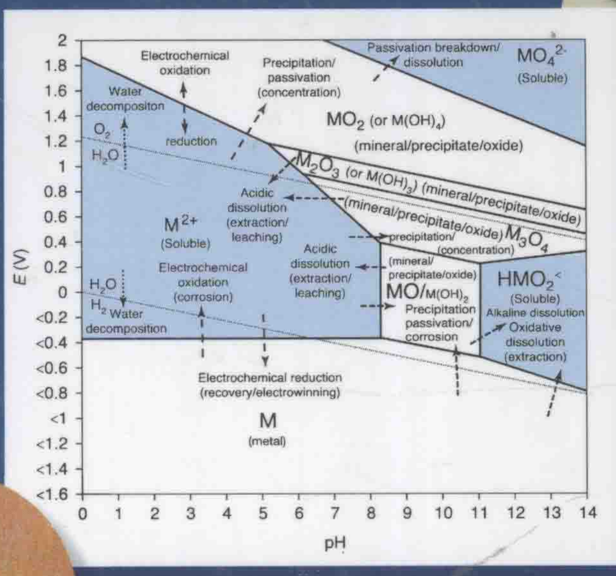
Hydrometallurgy

Fundamentals and Applications



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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Free, Michael.
Hydrometallurgy : fundamentals and applications / by Michael L. Free.
pages cm
Includes bibliographical references and index.
ISBN 978-1-118-23077-0 (hardback)
1. Hydrometallurgy. I. Title.
TN688.F74 2013
669.028'3–dc23

2013011235

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

PREFACE

This book provides a college-level overview of chemical processing of metals in water-based solutions. It is an expanded version of a previous textbook, *Chemical Processing and Utilization of Metals in Aqueous Media*, with two editions written by the author. The information in this book is relevant to engineers using, producing, or removing metals in water. The metals can take the form of dissolved ions, mineral particles, or metal. The material in each chapter in this textbook could be expanded into individual textbooks. It is clearly not comprehensive in its coverage of relevant information. Other resources, such as the four-volume series *Principles of Extractive Metallurgy* by Fathi Habashi, provide more details for specific metal processing methods. Thus, this text presents a condensed collection of information and analytical tools. These tools can be used to improve the efficiency and effectiveness with which metals are extracted, recovered, manufactured, and utilized in aqueous media in technically viable, reliable, environmentally responsible, and economically feasible ways.

The author expresses gratitude to his family, colleagues, teachers, and students who have contributed in various ways to the completion of this text.

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CHAPTER 1

Metals form the foundation for our modern standard of living. We would be living with Stone Age technology if we did not have metals.

INTRODUCTION

Key Chapter Learning Objectives and Outcomes

Understand the importance of metals
Know some important uses of metals
Know the value of metals
Understand how metal-bearing ore bodies can form
Understand how metals are naturally cycled in different forms on earth
Understand the importance of water in metal processing
Identify basic methods needed to produce metal from metal-bearing ore

1.1 THE IMPORTANCE OF METALS

Metals are needed for survival. Our bodies rely on metals to perform many vital functions. Iron is used to transport oxygen to cells. Calcium is needed for bones. Sodium and potassium are needed to regulate many necessary biological functions. Many other trace metals are needed for a variety of critical activities within our bodies.

Metals form a foundation for our modern standard of living. We use large quantities of metals to build transportation vehicles that range from bicycles and cars to ships and airplanes. We rely on metals for structural support for buildings, bridges, and highways. We need metals to build computers and electronic devices.

Hydrometallurgy: Fundamentals and Applications, First Edition. Michael L. Free.

Metals are also necessary to generate electricity. Metals are the foundation for the myriad of motors that mechanize our factories and homes. Metals are critical to our way of life. We would be living with Stone Age technology if we did not have metals.

Countless things are made of metal or have metal in them that is critical to their function. Metal items are found in nearly every part of the world, and metals are produced in a variety of locations around the world. A summary of metals and its uses is presented in Table 1.1. Worldwide production of metals is shown in Table 1.2.

The total annual value of raw metal produced in 2011 was estimated to be more than US$2 trillion. This is only the value of the raw metal. The value to the world economy is several times that amount when the value of the final products that use metal is considered.

Metals undergo continual cyclical processing on our planet as shown in Figure 1.1. Metal comes from the earth. Metals are continuously transported and transformed by geological processes.

Metals usually originate as minerals that are discovered, mined, and transformed into metal. All metal in use today is undergoing a very gradual or rapid process of corrosion or degradation. The process of corrosion is essentially a chemical transformation from the metallic form to the mineral or ion form. Atmospheric corrosion of metals leads generally to the formation of metal oxide minerals. The oxygen in the atmosphere and water causes the oxidation. Oxide mineral products of corrosion are often the same as the minerals in ores. Thus, metals are found in various forms depending on their position in the metal cycle. However, the time between metal cycle events can be enormous.

> Metals usually originate as minerals that are discovered, mined, and transformed into metal.

The processing paths used to produce individual metals are often very different. Many processing methods involve water or water-containing (aqueous) media. Thus, the term *hydrometallurgy* is often used to describe this topic. This textbook covers the fundamental principles of chemical metallurgy. It also presents many important methods of processing, utilizing, and evaluating metals and metal processes in aqueous media. This book includes many associated topics such as metal extraction, electrodeposition, power storage and generation, electroforming, environmental issues, economics, and statistics.

1.2 MINERAL DEPOSITION

Metals generally originate in the earth's crust as metal oxides, sulfides, and other minerals. Many metals such as aluminum, iron, calcium, sodium, magnesium, potassium, and titanium are abundant as shown in Table 1.3. In some locations, mineralization processes have concentrated specific metals. Metals such as

TABLE 1.1 Comparison of Selected Metals and Common Uses[a]

Metal	Symbol	Common Uses
Actinium	Ac	Thermoelectric power, source of neutrons
Aluminum	Al	Alloys, containers, aerospace structures, outdoor structures, also in ceramics as Al_2O_3
Antimony	Sb	Semiconductors, alloys, flame proofing compounds
Barium	Ba	Used mostly in nonmetallic forms such as barite and barium sulfate, specialty alloys
Beryllium	Be	Specialty alloys, electrodes, X-ray windows
Bismuth	Bi	Specialty alloys, thermocouples, fire detection, cosmetics
Cadmium	Cd	Specialty alloys, coatings, batteries, solar cells
Calcium	Ca	Used mostly in nonmetallic forms, reducing agent, deoxidizer, specialty alloys
Cerium	Ce	Used mostly in nonmetallic forms, catalysts, specialty alloys
Cesium	Cs	Catalyst, oxygen getter, atomic clocks
Chromium	Cr	Stainless steel, coatings, catalyst, nonmetallic forms in colorants, corrosion inhibitors
Cobalt	Co	High strength, high temperature alloys, magnets, nonmetallic forms as colorants
Copper	Cu	Electrical wiring, tubing, heat transfer applications, alloys such as bronze and brass
Dysprosium	Dy	Specialty magnets, specialty alloys, nuclear control applications
Erbium	Er	Nonmetallic forms as colorants
Europium	Eu	Specialty products in nonmetallic forms and alloys
Gadolium	Gd	Specialty products in nonmetallic forms and alloys
Gallium	Ga	Solar cells, semiconductors, neutrino detectors, specialty alloys, coatings
Gold	Au	Jewelry, bullion/investment tool, decoration, specialty coatings, alloys, coins
Hafnium	Ha	Specialty alloys, nuclear control rods
Holmium	Ho	Specialty alloys, filaments, neutron absorption
Indium	In	Specialty alloys, solar cells, thermistors, solder
Iridium	Ir	Specialty alloys and coatings, jewelry, electrodes
Iron	Fe	Steels, cast iron, many alloys—most widely used, lowest cost metal
Lanthanum	La	Specialty products in nonmetallic forms and alloys
Lead	Pb	Batteries, radiation shielding, cable covering, ammunition, specialty alloys
Lithium	Li	Heat transfer and specialty alloys, batteries, nonmetallic forms in glasses, medicine
Lutetium	Lu	Catalysts, specialty alloys
Magnesium	Mg	Specialty alloys, reducing agent, pyrotechnics, many nonmetallic form uses
Manganese	Mn	Steel and specialty alloys, nonmetallic form uses in batteries, colorants, chemistry

(continued)

TABLE 1.1 ***(Continued)***

Metal	Symbol	Common Uses
Mercury	Hg	Chlor-alkali production, amalgams, specialty uses
Molybdenum	Mo	Primarily used for steel alloys, catalysts, heating elements
Neodymium	Nd	Specialty magnets, lasers; also nonmetallic forms such as glass colorants
Neptunium	Np	Neutron detection
Nickel	Ni	Many specialty alloys, batteries, tubing, coatings, magnets, catalysts
Niobium	Nb	Specialty alloys, magnets
Osmium	Os	Specialty, high cost, hard alloys
Palladium	Pd	Alloys (decolorizes gold), catalysts, used for hydrogen gas purification
Platinum	Pt	Catalyst, jewelry, thermocouples, glass making equipment, electrochemistry
Plutonium	Pu	Nuclear weapons and fuel
Polonium	Po	Neutron source, satellite thermoelectric power
Potassium	K	Reducing agent, most uses in nonmetallic forms such as fertilizer
Praseodymium	Pr	Specialty alloys, nonmetallic forms such as glass colorant
Radium	Ra	Neutron source
Rhenium	Re	Specialty alloys, thermocouples, catalysts
Rhodium	Rh	Specialty alloys, thermocouples, catalysts, jewelry
Rubidium	Rb	Specialty alloys, catalysts, specialty glasses (nonmetallic)
Ruthenium	Ru	Specialty alloys, catalysts
Samarium	Sm	Magnets, specialty alloys, catalysts
Scandium	Sc	Specialty alloys
Silver	Ag	Jewelry, silverware, solder, batteries, antimicrobial applications, coins
Sodium	Na	Reagent in chemical reactions, batteries, used mostly in nonmetallic forms
Strontium	Sr	Specialty alloys, zinc refining, fireworks, glass colorant
Tantalum	Ta	Specialty alloys, capacitors, surgical appliances
Technetium	Tc	Radioactive tracers,
Thallium	Tl	Specialty alloys, photovoltaic devices
Thorium	Th	Specialty alloys, portable gas light mantles, catalysts
Thullium	Tm	Specialty alloys, radiation source if previously exposed
Tin	Sn	Specialty alloys, solder, coatings, semiconductors
Titanium	Ti	Aerospace alloys, corrosion resistant alloys, implants, paint pigment (TiO_2)
Tungsten	W	Filaments, alloys, tool steels and hard materials
Turbium	Tb	Dopant in solid-state devices, specialty alloys
Uranium	U	Nuclear fuel, nuclear weapons
Vanadium	V	Specialty steels, catalysts, nuclear applications

TABLE 1.1 (*Continued*)

Metal	Symbol	Common Uses
Ytterbium	Yb	Specialty alloys, radiation source
Yttrium	Y	Alloys, catalysts, nonmetallic colorant applications
Zinc	Zn	Galvanized metal coatings, alloys such as brass, solder, batteries, coins
Zirconium	Zr	Nuclear fuel canisters, corrosion resistant tubing, explosive primers

[a]References 1–3.

TABLE 1.2 World Metal Production, Price and Value Estimates Based on Data from USGS Mineral Commodity Summaries 2012[a]

Metal	Estimated Worldwide Production 2011 (metric tons)	Estimated Metal Price (2011), US$/kg	Estimated Total Value (Price × Production in US Dollars)
Aluminum	44,100,000	2.71	119,585,969,708
Antimony	169,000	13.45	2,272,757,336
Beryllium	240	447.54	107,409,775
Bismuth	8,500	25.57	217,376,926
Cadmium	21,500	2.75	59,125,000
Chromium	24,000	14.50	348,000,000
Cobalt	98,000	39.68	3,888,974,625
Copper	16,100,000	8.82	141,978,438,678
Gallium	95	700.00	66,500,000
Gold	2,700	51, 440.73	138,889,966,710
Indium	640	720.00	460,800,000
Iron/steel	1,100,000,000	1.32	1,455,058,533,036
Lead	4,500	2.49	11,210,565
Magnesium	780,000	5.18	4,041,094,380
Mercury	1,930	100.00	193,000,000
Molybdenum	250,000	76.94	19,235,432,880
Nickel	1,300,000	22.71	29,520,051,148
Niobium	63,000	41.00	2,583,000,000
Palladium	207	23, 470.54	4,858,400,758
Platinum	192	55, 301.04	10,617,800,216
Rhenium	49	2, 000.00	98,000,000
Silver	23,800	1, 108.93	26,392,557,155
Tin	253,000	25.35	6,414,383,033
Titanium	186,000	22.71	4,223,638,087
Zinc	12,400,000	2.20	27,337,463,348
Zirconium	1,410	64.00	90,240,000

[a]Reference 1.

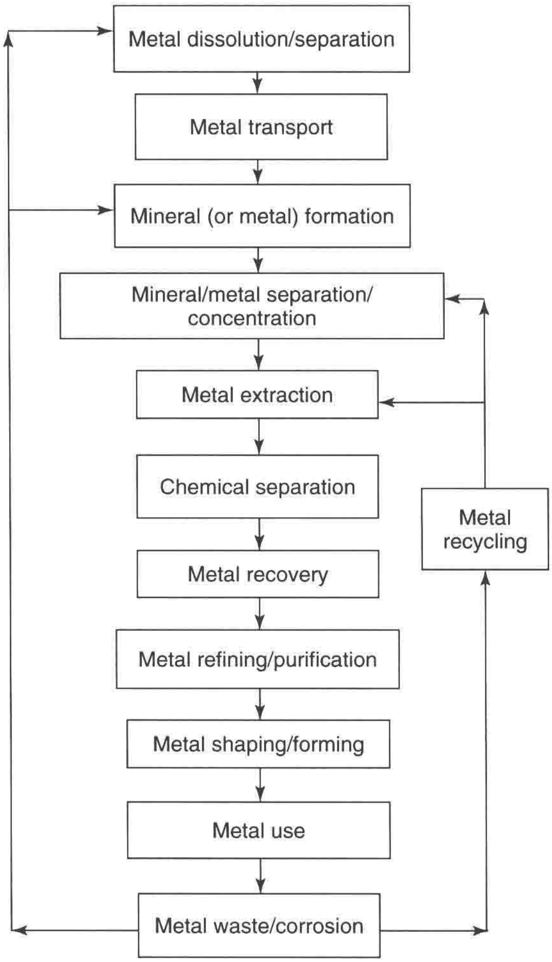

Figure 1.1 Overview of the general metal cycle.

manganese, barium, strontium, zirconium, vanadium, chromium, nickel, copper, cobalt, lead, uranium, tin, tungsten, mercury, silver, gold, and platinum are generally scarce. Economic extraction of scarce metals requires a suitable ore deposit.

Ores are natural materials containing a concentrated resource. An ore deposit or ore body contains a large volume of ore. Some rare metals and minerals must be concentrated by a factor of 1000 or more above their average natural abundance to form an economically viable ore body as indicated in Table 1.4 (see Appendix A for atomic weights to convert to an atomic basis).

The method of concentration within the earth's crust varies widely. It is dependent on the metal and associated mineral(s) as shown in Table 1.5. Some metals

TABLE 1.3 Abundance of Elements in the Earth's Crust[a]

Element	Abundance, %	Element	Abundance, %
Oxygen	46.4	Vanadium	0.014
Silicon	28.2	Chromium	0.010
Aluminum	8.2	Nickel	0.0075
Iron	5.6	Zinc	0.0070
Calcium	4.1	Copper	0.0055
Sodium	2.4	Cobalt	0.0025
Magnesium	2.3	Lead	0.0013
Potassium	2.1	Uranium	0.00027
Titanium	0.57	Tin	0.00020
Manganese	0.095	Tungsten	0.00015
Barium	0.043	Mercury	0.000008
Strontium	0.038	Silver	0.000007
Rare Earths	0.023	Gold	<0.000005
Zirconium	0.017	Platinum metals	<0.000005

[a]Reference 4.

TABLE 1.4 Enrichment Factors Necessary for Ore Body Formation[a]

Metal	Approximate Enrichment Factor from Natural Occurrence Level to Form Economical Ore Body
Aluminum	4
Chromium	3000
Cobalt	2000
Copper	140
Gold	2000
Iron	5
Lead	2000
Manganese	380
Molybdenum	1700
Nickel	175
Silver	1500
Tin	1000
Titanium	7
Tungsten	6500
Uranium	500
Vanadium	160
Zinc	350

[a]Reference 5.

Ores are natural materials containing a concentrated resource. An ore body is a local region in the earth's crust containing desired minerals in concentrations sufficient for commercial extraction.

TABLE 1.5 Methods of Metal/Metal-Bearing Mineral Deposition[a]

Mag.	Sub V.	Hydro.	Weath. Sed.	Plac.	Metas.
Aluminum	X				
Chromium	X	X			
Cobalt	X				
Copper	X	X	X	X	X
Gold	X	X	X		
Iron	X	X	X	X	X
Lead	X	X	X	X	
Manganese	X	X	X	X	
Molybdenum	X	X			
Nickel	X	X	X		
Silver	X	X	X		
Tin	X	X	X		
Titanium	X	X			
Tungsten	X	X	X		
Uranium	X	X			
Zinc	X	X	X	X	

Mag., magma crystallization;
Sub V, submarine volcanic exhalative processes;
Hydro., hydrothermal solution deposition;
Weath., weathering;
Sed., sedimentation;
Plac., placer deposition;
Metas., contact metasomatism.
[a]Reference 5.

Water can play an important role in ore body formation and metal processing.

such as chromium are concentrated by precipitation or crystallization in magma. Precipitation is dependent on solubility, which is dependent on temperature. As the magma cools, different local temperature zones are created. Each temperature zone may correspond to a specific mineral (or set of similar minerals) formation zone. Thus, temperature zones can create mineral zones or veins. This process is similar to the creation of ice crystals on a cold windshield. In such cases, a pure component leaves a mixture (air and water vapor) to form a pure deposit in locally enriched regions. A comparison of crystallization from magma and an air/water vapor mixture is illustrated in Figure 1.2.

Ore-grade aluminum deposits are formed by the dissolution and removal of contaminants such as silicates through extensive weathering. Weathering is most rapid in tropical environments. Correspondingly, most commercial aluminum deposits are in tropical regions).

Other metals such as silver and tin are concentrated hydrothermally. They are first dissolved in hydrothermal solutions within the earth's crust. Next, they are transported to regions where solution conditions change. Solution conditions can change due to changes in geological formations. Disruptions in rock layers