

New Research on Hydrometallurgy

by Ma Rongjun

Hunan Science & Technology Press

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# 湿法冶金 新研究

马荣骏 著



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赠书



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## **湿法冶金新研究**

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**内容简介** 本书收集了作者近三年来完成部分科研工作的 26 篇成果论文。全书分三部分,第一部分介绍了湿法冶金中的新工艺新进展;第二部分介绍了磁场效应在湿法冶金中的应用;第三部分是对稀土碳酸盐沉淀的研究。本书既有理论阐述,又有实用工艺介绍,内容新颖,反映了湿法冶金中一些前沿课题及发展趋势,是一本具有较高学术水平的专著。

本书可供从事冶金、化工及环境保护科研、设计、设备制造技术人员以及大专院校有关专业的师生参考使用。



作者简介

马荣骏, 1931 年 8 月生, 河北省大城县人, 1955 年毕业于东北工学院, 1955 ~ 1958 年于前捷克斯洛伐克 Košice 工业大学进行研究生学习。参加工作后, 历任课题组组长, 研究室正、副主任及研究所所长等职务。现任长沙矿冶研究院教授, 博士生导师, 东北大学、中南工业大学及湘潭大学兼职教授。

马荣骏长期从事湿法冶金及环境工程的科研工作, 40 多年来共完成了 60 余项科研项目, 有 28 项应用于工业生产, 产生了可观的经济与环境效益。80 年代以来, 有 20 多项科研工作通过了省、部级成果鉴定, 获全国科学大会奖 3 项, 国家科技进步二等奖 1 项, 省部级重大科技成果及科技进步一等奖 2 项、二等奖 5 项、三等奖 1 项、四等奖 3 项, 1998 年获湖南省环保系统科技进步二等奖 1 项。已申请了 2 项国家专利。培养研究生 12 名。

马荣骏编著出版了《钛的生产》、《有机萃取在冶金中的应用》、《溶剂萃取在湿法冶金中的应用》、《湿法炼铜新技术》、《工业废水的治理》、《离子交换在湿法冶金中的应用》、《湿法冶金新进展》、《湿法冶金新研究》等专著。参予主编及编写了《中国冶金百科全书》(有色冶金卷)及《溶剂萃取手册》。在国内外发表论文 160 多篇, 其中多篇被评为优秀论文, 并有多篇被 Ei、SCI 及 CA 等收录。

马荣骏治学严谨, 勤奋实干, 乐于奉献。1978 年被冶金部授予先进工作者称号, 1989 年被评为全国优秀环境科学工作者, 1991 年起享受政府特殊津贴, 对冶金工业做出了重要贡献。

## **A profile of Author**

Ma Rongjun was born in August 1931. His ancestral home is at Dacheng in Hebei province. He graduated from Northeast University of Technology in 1955. From 1955 to 1958 he studied as a graduate student at Kosice University of Technology in the former Czechoslovakia. After graduation he served successively as deputy director, and director of a department and director of a research institutes. At present he holds the positions of professor of Changsha Research Institute of Mining and Metallurgy under Ministry of Metallurgical Industry and is engaged as tutor for doctoral students, and part-time professor of Northeastern University, Central South University of Technology, and Xiangtan University. As a famous expert in hydrometallurgy and environmental engineering in China, Prof. Ma is concurrently director of Chinese Society of Rare Earths, director of Hunan Provincial Society of Rare Earths, deputy director of Academic Committee of physicochemistry of Metallurgical Process under Chinese Society of Nonferrous Metals, director of Hunan Provincial Society of Nonferrous Metals, director of Subsociety of Environmental Protection for Metallurgy, Chinese Society of Metals, managing director of Hunan Provincial Society of Environmental Science, and deputy director general of Hunan Provincial Branch of Environmental Engineering.

He has been engaged in research on hydrometallurgy and environmental protection engineering for more than 40 years, during which more than 60 projects were completed. More than 28 of the projects have been applied in commercial production. Since the 1980's, more than 20 research achievements have passed the provincial and ministerial - level appraisal. Among them three were awarded the prize of National Science Conference, one the 2nd prize of National Science and Technology Advances by the State, two the 1st prize and three the 2nd prize of key Achievements of Science and Technology by the Ministry of Metallurgical Industry and Hunan Province, one the 2nd prize of Science and Technology Advances by the Guangxi Zhuang Autonomous Region, one the 2nd prize and one the 3rd prize of Science and Technology Advances by

China Nonferrous Metals Industry Corporation, and three the 4th prize of Science and Technology Advances by Hunan Province.

So far Prof. Ma has compiled and published eight learned monographs, including Production of Titanium (Shanghai Science & Technology Press 1958), Applications of Organic Extraction to Metallurgy (Shanghai Science & Technology Press 1961), Applications of Solvent Extraction to Hydrometallurgy (Metallurgical Industry Press 1979), New Technology of Hydrometallurgy of Copper (Hunan Science & Technology Press 1985), Applications of Ion Exchange Technology to Hydrometallurgy (Metallurgical Industry Press 1991), Treatment of Industrial Wastewater (Central South University of Technology press 1991), for which he won the first award of excellent learned monograph, New Advance in Hydrometallurgy (Central South University of Technology Press 1996), New Research on Hydrometallurgy (Hunan science & Technology Press 1998).

In addition Prof. Ma has published over 160 research papers in periodicals or other publications at home and abroad, most of which have been widely cited, creating invaluable tremendous economic and social results. Prof. Ma has been appointed the member of editorial board of Nonferrous Metallurgy volume of Chinese Encyclopedia of Metallurgy, editing Hydrometallurgy in this volume, and editing part of Hand Book of Solvent Extraction.

Professor Ma is noted for his meticulous scholarship, diligence and spirit of working earnest. He was honoured with the titles of Advanced Worker and Excellent Researcher of Environmental Science. From 1991 on, he has been enjoying the special subsidies from the government. He makes a great contribution to China's metallurgical industry.

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# 前 言

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在可持续发展的战略方针指引下，基于能源、资源及环境保护的迫切要求，湿法冶金在金属及其化合物的制备、分离和提纯，矿产资源的综合利用，有价金属的回收和再生以及防止环境污染等方面，发挥了重要作用，并得到了迅速的发展。

为了总结经验，及时交流，互相促进，作者把近三年来，在湿法冶金中的部分最新研究成果，以26篇论文的形式，归纳整理成本书。按论文的内容，本书分为三部分。第一部分介绍了湿法冶金中的新工艺、新进展，第二部分介绍了磁场效应在湿法冶金中的应用，第三部分是对稀土碳酸盐沉淀的研究。本书力求反映当今该领域中的部分前沿课题及发展趋势，使其具有一定的创新性，以达到在理论及应用上，显示出应有的参考价值。

应该说明，书中的论文多是作者与合作者共同的劳动结晶，其中相当部分是柳松博士、马伟博士及李扬博士的学位论文成果，他们对该书的出版作出了重要贡献。还有一些同志在书稿的修改、校

## 湿法冶金的新研究

对中给予了热情的帮助，特别是刘业翔院士、刘宝琛院士、余永富院士及朱俊士教授，对该书写出了中肯、宝贵的推荐出版评审意见。湖南省科委为本书出版给予了经费资助及大力支持，作者对此致以衷心的感谢。

由于作者水平所限，书中错误敬请有关专家及广大读者批评指正。

**马荣骏**

1998年8月



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# 1 湿法冶金的新工艺、新进展



# 沉淀过程的理论和应用的新进展\*

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**摘要** 论述了难溶物质在水溶液中沉淀过程的理论,其中包括成核、晶体生长、聚沉和陈化等过程。并介绍了沉淀过程研究和应用的新进展。

**关键词** 沉淀过程 沉淀理论 沉淀应用

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沉淀过程是一个在分析、冶金、化工及应用化学中古老的单元过程。由于该方法简单易行,所以一直被广泛应用。从微观上来看,沉淀过程发生的变化极为复杂。近些年来,对该过程的理论研究较少,而它又在高新技术的纳米原材料的制备中得到应用。鉴于其重要性,本文就沉淀过程的理论及研究中的新应用做一些介绍。

## 一、沉淀理论<sup>[1,2]</sup>

从水溶液中析出电解质沉淀的过程主要涉及成核、晶体生长、

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\* 本文首次交流于1998年全国冶金物化学术会议(上海),并收入了该学术会议的论文集,合作者:柳松。



聚沉、陈化等过程。

### (一) 成核过程

水溶液中的成核过程理论是由蒸气相形成液滴过程的成核理论类推而来，成核分均相成核与异相成核。均相成核是由于均相晶核的形成而引起的，而异相成核则起源于溶液中的杂质。

按照经典热力学成核理论，均相晶核被当作具有临界大小的聚集体，当浓度低于临界水平时，离子群可逆地生长或分解；当浓度达到或超过临界水平时，形成均相晶核。

从溶液中析出电解质沉淀  $A_xB_y$  的热力学驱动力是  $nTR\ln S$  (这里  $n=x+y$ ,  $R$  是摩尔气体常数,  $T$  是热力学温度,  $S$  是饱和比, 等于电解质的活度  $\alpha$  除以电解质的溶解度  $C$ )。而固相沉淀的形成, 又必须克服产生的新固相的表面能。对于均相成核, 沉淀过程的自由焓变化:

$$\Delta G = -nRT\ln S + A\sigma \quad (1)$$

这里  $A$  是界面面积,  $\sigma$  是电解质固相与溶液之间的界面张力。

对于异相成核, 其过程的自由焓变化:

$$\Delta G' = -nRT\ln S + A\sigma' \quad (2)$$

这里  $\sigma' < \sigma^{(3)}$ , 所以  $\Delta G' < \Delta G$ , 从能量的角度上看, 异相成核比均相成核要容易进行。实际情况是: 当溶液的饱和比较低时, 异相成核占优势; 当溶液的饱和比较高时, 均相成核占优势。

若沉淀颗粒是球形的, 由 (1) 式可得晶核的临界半径:

$$r^* = \frac{2\sigma V}{kT\ln S} \quad (3)$$

这里  $V$  是分子体积,  $k$  是玻尔兹曼常数。

此过程的活化能

$$\Delta G = \frac{16\pi\sigma^3 V^3}{3K^2 T^2 \ln^2 S} \quad (4)$$

其中 (3) 式就是著名的 Gibbs-Thompson 方程<sup>[4]</sup>。

关于沉淀过程中的稳态成核速度  $J$ , 表达式有一些不同, 按机械力学的观点<sup>[4]</sup>: