

**FIRE Compendium Series Vol. 2A**

# **Corrosion of Refractories - The Fundamentals**

Jacques Poirier and Michel Rigaud

Wear by corrosion of refractory materials remain a major concern for plant operators, manufacturers of refractories, installers and refractory engineers involved in R&D and Education in this field of expertise. The entire subject will be covered in within three volumes. The other will present an in-depth compilation of the major testing tests and characterization methods (volume 2B) and the impact of corrosion on plants availability and products quality, revealing what can be learned from post-mortem analysis, through pertinent case studies (volume 2C).

The first volume (volume 2A) on the Fundamentals is being treated at the macro-, meso- and microscopic scale, focusing on degradation mechanisms including thermal aspects; chemical aspects and transfer of materials; phase changes and mechanical aspects; and coupling between all those aspects. It does provide the readers with the conceptual tools for a clear understanding of the degradation phenomena frequently observed, providing the insights for improving the performances of those materials (inserted in complex linings) and exposed to increasingly harsh environment.

Seven authors have been recruited by FIRE, lead by J. Poirier and M. Rigaud, to cover the seven chapters: 1- Features of refractory corrosion by J. Poirier and M. Rigaud; 2- Thermodynamics by M. Rigaud, J. Smith, In-Ho Jung and J. Poirier; 3- Kinetics by Y-B Kang; 4- Wettability by N. Eustathopoulos; 5- Reactions and mechanisms of corrosion by J. Poirier; 6- Thermal, chemical and mechanical couplings by É. Blond; 7- Impact of operating conditions on refractory lining wear by J. Poirier and M. Rigaud.

The content of the book has been reviewed by fourteen fellow experts (industrials and academics) worldwide. It represents a major contribution to grasp in depth the main principles to address the major issues concerning the corrosion of refractories.

# Table of Contents

<b>Foreword</b>	<b>vii</b>
<b>Preface</b>	<b>viii</b>
<b>The Authors</b>	<b>xi</b>
<b>F.I.R.E.</b>	<b>xiii</b>

## **Chapter 1** **Features of refractory corrosion**

<b>1. Introduction</b>	<b>1</b>
<b>2. Issues of refractory corrosion and industrial sectors affected</b>	<b>8</b>
<b>3. Degradation factors</b>	<b>12</b>
<b>4. Characteristics and durability of refractories</b>	<b>18</b>
<b>5. Designing the microstructure for corrosion resistance</b>	<b>19</b>
<b>6. Fundamentals and tools: thermodynamics and kinetics, wettability, post mortem examinations, experimental methods</b>	<b>24</b>
6.1. Thermodynamics	26
6.2. Kinetics	27
6.3. Wettability and refractory infiltration by liquids	27
6.4. Industrial expertise, observation of operational corrosion, “post mortem” sample examination	32
6.5. Laboratory study of corrosion phenomena	33
<b>7. Conclusion</b>	<b>37</b>
<b>8. References</b>	<b>38</b>

## **Chapter 2** **Thermodynamics**

<b>1. Introduction</b>	<b>43</b>
<b>2. Basic Knowledge of Thermodynamics</b>	<b>44</b>
2.1. Gibbs Energy	45
2.2. Stability and Equilibrium	46
2.3. Thermodynamics of Solutions	50

*Contents*

2.4. Solubility limits	55
<b>3. Equilibrium Diagrams</b>	<b>56</b>
3.1. Ellingham Type Diagrams	57
3.2. Area Predominance diagrams	60
3.3. Phase Diagrams of Two Components	62
3.4. Phase Diagrams of Three Components	67
<b>4. Computational Thermodynamics</b>	<b>80</b>
4.1. Thermodynamic Packages and Databases	80
4.2. Refractory Corrosion Applications	84
<b>5. Microstructure and phase transformation of corroded refractories explained by phase diagrams and thermodynamics</b>	<b>94</b>
5.1. Introduction	94
5.2. Microstructural transformation of phases predicted by thermodynamics	95
5.3. Crystallization paths explained by microstructures and thermodynamics	98
5.4. Corrosion of refractories interpreted by microstructures and thermodynamics	104
<b>6. References</b>	<b>114</b>

**Chapter 3**  
**Kinetics**

<b>1. Introduction</b>	<b>121</b>
<b>2. Basic knowledge of the kinetic theory</b>	<b>123</b>
2.1. Definition of reaction rate	124
2.2. Homogeneous reaction	131
2.3. Heterogeneous reaction	140
<b>3. Experimental studies for dissolution kinetics</b>	<b>150</b>
3.1. Experimental techniques	152
3.2. Uncertainty and limit of the experimental approaches	161
<b>4. Modeling studies for dissolution kinetics</b>	<b>164</b>
4.1. Different modeling techniques	165
4.2. Coupling with thermodynamics/phase equilibria	176
4.3. Perspective of the modeling approach	179

<b>5. Summary</b>	<b>180</b>
<b>6. References</b>	<b>180</b>

## Chapter 4

### Wetting and infiltration of refractories by liquid metals and oxides

<b>1. Introduction</b>	<b>187</b>
<b>2. Fundamental equations of wetting and capillarity</b>	<b>188</b>
2.1. Surface energy and adhesion energy	188
2.2. Young and Young-Dupré equations	189
2.3. Capillary Pressure-Laplace's equation	192
2.4. Effect of surface roughness and surface heterogeneities on the contact angle	194
2.5. Wetting kinetics of non-reactive liquids	198
<b>3. Data of contact angles for non-reactive liquid-solid systems</b>	<b>203</b>
<b>4. Effects of interfacial reactions</b>	<b>207</b>
4.1. Wetting with formation of a new compound at the interface	207
4.2. Dissolutive wetting	211
<b>5. Methods of measuring the contact angle</b>	<b>212</b>
<b>6. Infiltration</b>	<b>214</b>
6.1. Non-reactive infiltration-Thermodynamics	214
6.2. Non-reactive infiltration-Kinetics	216
6.3. Effects of interfacial reactions	221
<b>7. References</b>	<b>226</b>

## Chapter 5

### Reactions and Mechanisms of Corrosion

<b>1. Introduction</b>	<b>229</b>
<b>2. Influence of temperature</b>	<b>229</b>
2.1. Maximum temperature of usage	229
2.2. Effect of phase transformations	238
<b>3. Influence of the liquid phase characteristics</b>	<b>242</b>
3.1. Slag characteristics: roles, structures and properties	243
3.2. Marangoni Effect	258
3.3. Transport Mechanism	260

*Contents*

3.4. Reaction inventory and fundamental mechanisms	271
<b>4. Influence of the gaseous environment</b>	<b>297</b>
4.1. Corrosion by gas with formation of gaseous, liquid or solid products	297
4.2. Fundamental mechanisms of corrosion with formation of gaseous, liquid or solid products [74]	299
4.3. Reaction inventory and key factors of corrosion	303
<b>5. How to limit the corrosion? (further details in volumes 2B and 2C)</b>	<b>328</b>
<b>6. References</b>	<b>330</b>

**Chapter 6**

**Thermal, chemical and mechanical couplings**

<b>1. Introduction</b>	<b>337</b>
<b>2. Definition of the System and State Variables</b>	<b>340</b>
2.1. Equilibrium, steady-state and evolution	341
2.2. State variables	342
2.3. Local state postulate	343
<b>3. Balances/Conservation Laws</b>	<b>344</b>
<b>4. First Law of Thermodynamics</b>	<b>346</b>
<b>5. Second Law of Thermodynamics</b>	<b>348</b>
5.1. Chemical diffusion	350
5.2. Chemical reactions and phase changes	350
<b>6. From entropy to state and evolution laws</b>	<b>353</b>
6.1. Entropy for continuous reactive open media	353
6.2. From entropy to behavior law – Clausius-Duhem inequality	355
6.3. State law	358
6.4. Evolution law	362
6.5. Exchange laws / fluxes	365
6.6. Heat equation and heat source expressions	366
<b>7. Examples of multiphysical modelling in the refractory field</b>	<b>368</b>
7.1. Reactive mass transport	369
7.2. Stress / Strain induced by mass transport	378
7.3. Stress / Strain induced by chemical reactions and phase change	388

<b>8. Basics on numerical resolution of multi-physics problems</b>	<b>393</b>
8.1. Time integration and spurious oscillation	393
8.2. The different numerical schemes to solve multi-physics problems	398
<b>9. Further reading</b>	<b>402</b>
<b>10. References</b>	<b>404</b>

## **Chapter 7**

### **Impact of operating conditions on refractory lining wear**

<b>1. Introduction</b>	<b>409</b>
<b>2. Adjusting the thermal gradient of the refractory lining</b>	<b>409</b>
2.1. Thermal gradient effect on refractory lining corrosion	410
2.2. Operating conditions to form a solid slag protective layer at the hot face of the lining	415
2.3. Lab experiments: formation of a solid slag crust / dissolution of refractory lining	421
2.4. Discussion	429
<b>3. Composition adjustment of the penetrant fluid</b>	<b>431</b>
<b>4. Reducing the reactivity by changing the wetting characteristics</b>	<b>436</b>
<b>5. Selecting refractory with a less porous and less permeable microstructure</b>	<b>437</b>
<b>6. Limit the penetration of the liquids into the refractory porosity by new precipitated solids that clog the pores</b>	<b>440</b>
6.1. Interaction between slag and matrix	442
6.2. Interaction between slag and alumina aggregates	443
<b>7. Using glazing or coating</b>	<b>444</b>
<b>8. Conclusion</b>	<b>446</b>
<b>9. References</b>	<b>446</b>
<b>Index</b>	<b>450</b>