#### FIRE Compendium Series Vol. 2B

# **Corrosion of Refractories -Testing and Characterization Methods**

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.

This second volume on the theme of corrosion is yet to be followed by volume 2C : The Impact of Corrosion.

The aims are 1) to describe how to evaluate corrosion damages under laboratory conditions and to establish correlations with in-plant testing; 2) to describe how to determine the materials characteristics once corroded, introducing the description of in-situ and advanced methods, with a specific section on castables; 3) to review ways to minimize corrosion damages selecting the appropriate material and the best installation procedure and adopting key standard operating procedures; 4) to provide the tools to learn from theories, concepts and various disciplines.

Seven authors have been recruited by FIRE, to cover the subject in three main chapters: I Testing Methods: 1.1 Laboratory Testing Methods: 1.1.1 Tesing up to 1600C – P. Quirmbach; 1.1.2 Testing up to 2000C – P. Piluso 1.1.3 Testing Composite Materials – F. Rebillat 1.2 In-Plant testing vs Full Testing – M. Rigaud,T. Vert.

II Characterization Methods for Corroded Samples. 2.1 Traditional Methods – M. Rigaud; 2.2 Insitu and Advanced Methods – J. Poirier; 2.3 Specific Methods for Castables – C. Worhmeyer.

III Ways to Minimize Corrosion Damages. 3.1 Ways to Minimize L-S Attack – M. Rigaud; 3.2 Ways to minimize G-S Attack – J. Poirier; 3.3 Ways to learn from Experience – M. Rigaud

The content of the book has been outlined and reviewed by fellow experts (industrials and academics). It represents a major contribution to appreciate the impact of corrosion of refractories on the plant availability and quality of products

## **Table of Contents**

Prologue	v
Foreword	vii
Preface	viii
List of the Editorial Review Board Members	x
The Authors	xi
F.I.R.E.	xiv

#### Chapter 1

#### **Testing Methods for Corrosion**

1.	Laboratory Testing Methods up to 1600 °C	1	
1.1.	Introduction	1	
1.2.	Corrosion provoked by oxide melts and metal melts		
	1.2.1. Pill test and disc test	2	
	1.2.2. Crucible test	2	
	1.2.3. Induction furnace test	4	
	1.2.4. Test with rotating sample – Finger test by dipping	9	
	1.2.5. Test with rotating slag – Rotary furnace test	10	
1.3.	Corrosion provoked by salts	12	
1.4.	Corrosion provoked by gases	13	
	1.4.1. Test procedure in lab scale:	14	
	1.4.2. Corrosion caused by oxidative gases – oxygen and steam		
	in contact with silicon carbide	15	
	1.4.3. Carbon monoxide corrosion	16	
	1.4.4. Hydrogen corrosion	18	
1.5.	Outlook	21	
1.6.	References	21	
2.	Laboratory Testing methods up to 2000 °C	23	
2.1.	Introduction	23	

#### Contents

2.2.	Refractories for the Nuclear Industry	24
2.3.	VULCANO facility 2.3.1. The furnace 2.3.2. Test sections	<b>27</b> 27 29
2.4.	KROTOS facility	32
2.5.	VITI facility	35
2.6.	References	39
3.	Laboratory testing Methods of Composite Materials	41
3.1.	Introduction	41
3.2.	Description of composite materials.	41
3.3.	<ul> <li>Methodology of oxidation/corrosion study from the single constituents up to the composite architecture</li> <li>3.3.1. On single constituents</li> <li>3.3.2. Reactivity between constituents in a composite during self-healing</li> <li>3.3.3. On composite materials</li> <li>3.3.4. Complemental methods to quantify the degradation progression</li> </ul>	<b>44</b> 44 47 49 52
3.4.	Coupling between oxidation/corrosion and mechanical loading	55
3.5.	Oxidation/corrosion for CMC coated with an EBC	63
3.6.	Conclusion	66
3.7.	References	66
4.	Panel In-plant Testing versus Full Testing	75
4.1.	References	76

### Chapter 2

## Characterization Methods of Corroded Samples

1.	Traditional characterization Methods	77
1.1.	Introduction	77

Contents	
00111011103	,

1.2.	Observation of the corroded refractory at a macroscopic scale: that of the refractory lining (from ten meters to ten	70		
	centimeters)	79		
1.3.	Observation of the corroded refractory at a mesoscopic scale: that of the refractory sample (from ten centimeters to ten millimeters)			
1.4.	Analysis of the corroded refractory at micro and nanoscopic scale: that of the microstructure and atomic structure of the material, from a tenth of a millimeter $(10^{-4} \text{ m})$ to the			
	nanometer (10 <sup>-9</sup> m)	90		
	1.4.1. Chemical analysis	90		
	1.4.2. Characterisation of the porosity	93		
	1.4.3. Characterization of the microstructure by optical	00		
	microscopy	99		
	1.4.4. Characterization of microstructure by	101		
	cathodoluminescence (CL) microscopy	101		
1.5.	Scanning electron microscopy (SEM) and X-ray			
	spectroscopy analysis (EDS, WDS)	103		
	<ul><li>1.5.1. Secondary electron and backscattered electron imaging</li><li>1.5.2. Quantitative image analysis of microstructures</li><li>1.5.3. Analysis by energy dispersive X-ray spectroscopy (EDS)</li></ul>	105 109		
	and by wavelength-dispersive X-ray spectroscopy (WDXS or WDS)	110		
1.6.	Electron Probe Microanalyzer	115		
1.7.	Transmission electron microscopy (TEM)	117		
1.8.	Analysis of refractory structures by X-Ray diffraction	120		
1.9.	Thermal analyses	125		
	1.9.1. Thermogravimetric analysis	125		
	1.9.2. Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)	127		
1.10	Conclusion	129		
1.11.	References	129		
2.	In situ and Advanced Characterization Methods	134		
2.1.	Introduction	134		

#### Contents

2.2.	2. Transport properties (permeability and capillary suction		
		urements)	135
	2.2.1.	Transport properties required for the simulation of slag	
		impregnation	135
		Intrinsic permeability determination	138
	2.2.3.	Determination of capillary curve parameters	151
2.3.		no-physical properties of molten oxides (density, ity and surface tension) using levitation techniques	153
2.4.	Corro	sion kinetics using High Temperature X Ray	
		ction (HT XRD)	160
	2.4.1.	Corrosion of alumina by lime/alumina/silica slag –	
		Thermodynamics and ex situ analyses	160
	2.4.2.	Corrosion tests and time-resolved high-temperature	
		X-ray Diffraction analyses	166
	2.4.3.	Applications	167
2.5.	The cl	naracterization of phase transformations using Raman	
	spectr	oscopy	171
	2.5.1.	Ex-situ Raman analysis: application on olivine	173
	2.5.2.	High temperature in-situ Raman analysis: application on zirconia and Yttria	175
2.6.	Concl	usion	179
2.7.	Refere	ences	179
3.	Specif	ic methods to characterize castables	186
3.1.	Metho	ods to characterize castables during dry and wet mixing	
	and cu	aring process:	187
	3.1.1.	Castable dry-mix:	187
	3.1.2.	Castable wet-mix:	189
3.2.	Castal	bles during hardening and curing process	198
		Cup test	198
	3.2.2.	Ultrasonic profile	198
	3.2.3.	Exothermal profile	203
		pH profile and ion concentration in the pore water	204
	3.2.5.	Electrical conductivity profile	205
		Early age strength measurements	206
	3.2.7.	Early age shrinkage measurement (during curing) !!	207

3.3.	Metho	ds to characterize castables during the dry-out and	
	first h	eating process	209
	3.3.1.	Permeability and Pressure measurements	209
	3.3.2.	Permanent Linear Change (PLC)	215
	3.3.3.	Restrained PLC	217
	3.3.4.	Thermal Expansion	218
	3.3.5.	Strength after firing, measured at room temperature alert	220
		Microstructural changes	220
	3.3.7.	Young's Modulus measurement during firing	222
	3.3.8.	Resonance Frequency Damping Analysis (RFDA)	224
	3.3.9.	Resistance to thermal shocks and to thermal cycling:	228
	3.3.10	. Thermal cycling test in a temperature gradient	230
3.4.	Metho	ds to characterize castables in contact with slag and	
	metals	;	230
	3.4.1.	Slag wettability	230
	3.4.2.	Impact of temperature and chemical gradient on Young's	
		modulus	233
	3.4.3.	Castable dissolution kinetics in slag	235
	3.4.4.	Corrosion as a function of furnace pressure	236
	3.4.5.	Corrosion tests for castables for aluminium metal	
		contact applications	237
	3.4.6.	Thermal shock test for castables with slag penetration layer	238
3.5.	Simula	ation methods	239
	3.5.1.	Finite Element Method (FEM)	239
	3.5.2.	Thermodynamic calculation software	240
3.6.	Summ	ary	240
3.7.	Refere	nces	240

#### **CHAPTER 3**

### Ways to minimize Corrosion Damage

1.	The S-L-G Characteristics	247
1.1.	The solid (S) interface	247
1.2.	Molten metal characteristics	250
1.3.	Molten slag characteristics	252

1.4.	The Molten salt characteristics	254
1.5.	Gaseous environment characteristics	257
2.	Ways to minimize L-S Attacks	259
2.1.	Ways to minimize penetration	259
	2.1.1. Texture adjustments	260
	2.1.2. Compositional changes of the refractory materials	260
	2.1.3. Compositional changes of the penetrants	262
	2.1.4. Adjusting the gradient of temperature at the hot face	262
2.2.	Ways to minimize Dissolution	263
	2.2.1. Texture adjustments	264
	2.2.2. Compositional changes of the refractory materials.	264
	2.2.3. Compositional changes of the liquid characteristics	265
	2.2.4. Adjusting the Gradient of Temperature at the hot Face	266
3.	Ways to minimize G – S Attacks	268
3.1.	Texture Adjustments	268
3.2.	Appropriate Selection of Refractory Materials	269
3.3.	Adjusting the Environmental Conditions	269
3.4.	Adjusting the Thermal Gradient at the Interface	270
4.	Concluding Remarks: Ways to learn from Experience	270
5.	References	271
Inde	x	275