## **Table of Contents**

Acknowledgements	3
Table of Contents	4
Abbreviations	8
1. Roman cements key materials of the built heritage of the nineteenth/early twentieth centuries	9
1.1 History	10
1.2 Definition	11
1.3 Raw materials and production	14
1.4 Historic Roman cement mortars	19
1.5 Conservation problems	27
2. Calcination of marls to produce Roman cements	30
3. Hydration of Portland cement	30
3.1 Early hydration of OPC	32
3.2 The late period of OPC hydration	36
3.2.1 Composition and structure of C-S-H	37
3.2.2 Morphology of C-S-H	38
3.3 Microstructure of the OPC pastes and mortars	39
4. Study Aims	41
5. Materials investigated	43
5.1 Cements	43
5.2 Cement pastes - design, setting and strength development	48
5.2.1 Setting	49
5.2.2 Compressive strength	50
5.3 Mortars – design and curing conditions	53
5.4 Historic Roman cement mortars	55
6. Experimental methods used	57
6.1 X-ray diffraction of cement materials	57
6.1.1 X-Ray diffraction of cement powders	57
6.1.2 In-situ X-ray diffraction of pastes	58

6.2 Mercury intrusion porosimetry	59
6.2.1 Physical basis of the method, its strength and limitations	59
6.2.2 Cement paste drying	60
6.3 Specific surface area	61
6.3.1 The BET equation	62
6.3.2 The t-method	63
6.3.3 The water vapour surface area	64
6.4 Thermal analysis	64
6.5 Scanning electron microscopy (SEM)	64
6.6 Adhesion	66
7. Results and discussion	67
7.1 Hydration during wet-air curing	67
7.1.1 Growth of crystalline hydrates and consumption of the components of origin cements in the hydration process as measured by the in-situ XRD	al 67
7.1.1.1 Initial stage of hydration	67
7.1.1.2 Late stage of hydration	81
7.1.1.3 Hydration of Roman cement mortars	87
7.1.2 The development of specific surface area in Roman cement pastes	90
7.1.2.1 Experimental approach	90
7.1.2.2 Interpretation of the measurement data	93
7.1.2.3 Specific surface area of Roman cement pastes and mortars	95
7.1.3 Thermal analysis	101
7.1.3.1 Identification of hydrated products in Roman cement pastes	101
7.1.3.2 Quantification of the hydrated product content	106
7.1.3.3 The degree of hydration α	109
7.1.4 The microstructure of Roman cement pastes by means of SEM-EDX analysis	116
7.1.5 Pore structure of hydrated Roman cements as measured by mercury intrusion porosimetry (MIP)	n 121
7.1.5.1 Pore structure of Roman cement pastes	121
7.1.5.2 The influence of water content on the pore structure of the pastes	126
7.1.5.3 Porosity structure of Roman cement mortars	128
7.2 Hydration on exposure to real-world environments	129
7.2.1 Hydration of mortars in different curing conditions	129
7.2.2 Porosity of historic mortars	132
7.2.3 The influence of different porous substrates on the hydration of mortars	137

7.2.4 The influence of water repellent treatment on hydration			138
7.3 The influence of hydra	tion on the adhesi	ion of Roman cement repair morta	rs 140
7.3.1 The adhesion of Roman cement repairs and the effect of curing conditions			
7.3.2 The influence of mortar composition on the adhesion			142
7.3.3 Adhesion of subseque	ent layers of fresh i	nortar	143
Conclusions			146
List of Figures			150
List of Tables			156
List of Equations			158
References			159

embled the cast and economic minusanting of February and February on the

external farades of buildings, Roman sentings white the rest of the external