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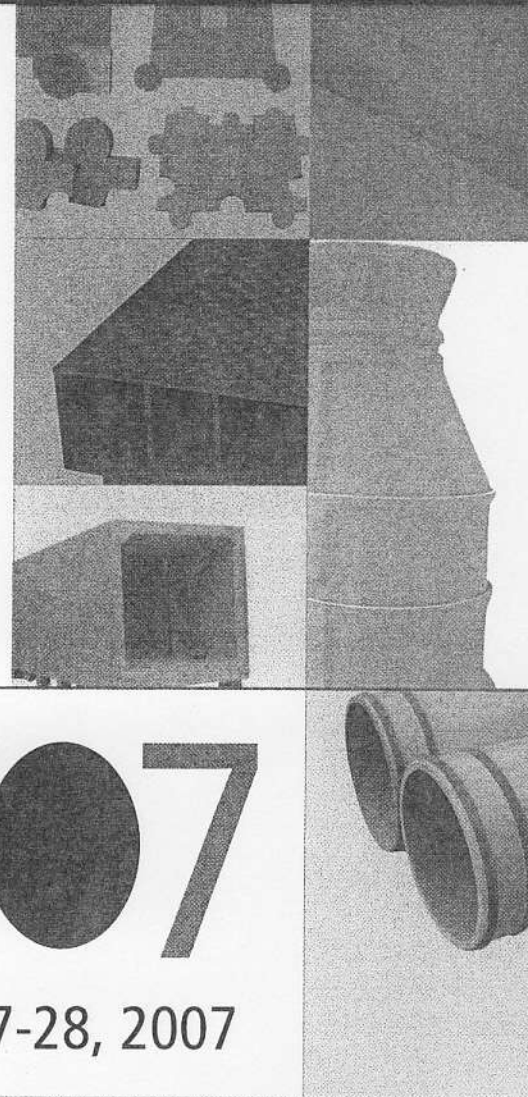
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Edited by **Kyu-Seok Yeon**
Kangwon National University



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Edited by
Kyu-Seok Yeon
Kangwon National University

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CONTENTS

Volume I

PART 1 Recent Research and Development Trends

- 3 Cement-Concrete and Concrete-Polymer Composites: Two Merging Worlds
Dionys Van Gemert / Belgium
- 17 From Nanomonitoring to Nanotechnology of Concrete-Polymer Composites; Searching for Synergy
Czarnecki Lech / Poland
- 29 State of the Art in Concrete Polymer Materials in the U.S.
David W. Fowler / U.S.A.
- 37 Recent Research and Development Trends of Concrete-Polymer Composites in Japan
Yoshihiko Ohama / Japan
- 47 Research and Development of Concrete-Polymer Composites in China
Peiming Wang and Ru Wang / China
- 55 Recent Progress of the Researches and Applications of Concrete-Polymer Composites in Korea
Kyu-Seok Yeon / Korea
- 67 Current Rehabilitation Technologies for Sewerage in Japan
Makoto Kawakami, Hiroyuki Sakakibara and Takefumi Matsumura / Japan
- 75 Recent Status of Application and Procedures for Barrier Penetrants on Japan
Kaori Nagai, Kenji Kano, Atsushi Shirai, Haruka Ogawa and Yoshihiko Ohama / Japan

PART 2 Properties of Concrete-Polymer Composites

- 85 Study on Absorption of Polymer on Cement in Fresh Paste
Shiyun Zhong / China
- 95 Effect of Water-Soluble Polymers on Microstructures in Cement Mortars
Elke Knapen and Dionys Van Gemert / Belgium
- 105 Effect of Polymer-Cement Ratio on the Mortar Performance
Nazmiye Parlak, Baris Ozer and M. Hulusi Ozkul / Turkey
- 113 Effect of Latex and Fiber Addition on Mechanical and Durability Properties of Sintered Fly Ash Lightweight Aggregate Concrete Mixtures
Neelamegam M., Dattatreya J.K. and Harish K.V. / India
- 123 Effect of Polycarboxylic Ether on the Early Age Strength of Self-Compacting Concrete with High Volume Fly Ash
Sukumar Biju and K. Nagamani / India
- 129 Study on the Bonding Performances and the Mechanism between Styrene-Butadiene Rubber Latex Modified Mortar and Substrate
Yingjun Mei, Peiming Wang and Naixing Liang / China

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- 137 Study on Polyacrylic Ester Latex-Modified Mortar
Ru Wang and Peiming Wang / China
- 145 Study on the Relation between Curing Age, Curing Condition and Adhesive Strength of EVA Modified Mortars to Tile
Danhua He / China
- 151 Experimental Research for Complex Early Strength Agent and Fly Ash on the Performance of Concrete
Tao Ye, Zhichu Huang and Zhiyin Zhang / China
- 157 Adhesion Strength and other Mechanical Properties of SBR Modified Concrete
Bogumila Chmielewska / Poland
- 167 Research on Mechanical Properties of Slag-Based Geopolymer Cement
Qing Wang, Zhitong Sui, Lei Liu and Changpeng Wu / China
- 173 Dry Shrinkage and Strength Properties of High-Fluidity Polymer-Modified Paste
Myung-Ki Joo and Youn-Su Lee / Korea
- 181 Mechanical Properties of Geopolymer Concrete under High Temperature
Qing Wang, Zhitong Sui, Lei Liu and Changpeng Wu / China
- 189 Temperature Dependence of Cleavage Bonding Properties between CFRP Sheets and Concrete
Kimio Fukuzawa, Masakazu Mitsui, Tatsuya Numao and Isao Funakawa / Japan
- 199 Research into Prediction of Antifreeze Critical Strength of Infant Age Concrete under Low Temperature
Jun Liu and Runqing Liu / China
- 207 Spalling Resistance of High Strength Concrete Containing Hybrid Organic Fibers
Cheon-Goo Han, Seong-Hwan Yang, Min-Cheol Han, Young-Sun Heo, Dong-Gyu Lee and Yong-Won Song / Korea
- 215 Study of Cement Mortars Modified by Epoxy Emulsion (EEM)
Liguang Xiao, Haijun Li and Jing Luo / China
- 223 Dry Shrinkage and Pore Size Distribution of Polymer-Modified Mortar
Shiyun Zhong, Feng Wang, Zhuan Yan, Wenyan Wang, and Zhiyuan Chen / China
- 233 Adsorption of Polymer Particles on Cement in Polymer Modified Cement
Sakai Eisuo, Rika Okudaira and Masaki Daimon / Japan
- 239 Microstructure of PCC Effects of Polymer Components and Additives
Andrea Dimmig-Osburg / Germany
- 249 Effect of Polymer on Performances of Lightweight Aggregate Concrete
Liguang Xiao, Qiang Zhou, Dexin Huang and Rui Ding / China
- 255 Preliminary Exploration on Properties of Slag Micro Powder Produced by Vertical Grinding Mill and Its Application in Concrete
Yanhua Shen / China
- 265 Compressive Strength of Pozzolan-Modified Plastering Materials: Testing, Modeling and Predictions
Damian Kachlakev / U.S.A.
- 275 Study on the Basic Properties of the Polypropylene Fibers Reinforced Polymer Mortar and Concrete
Xuedong Xu and Zhijin Zhong / China
- PART 3 Development Techniques of Concrete-Polymer Composites
- 285 Contribution of C-PC to Sustainable Construction Procedures
Dionys Van Gemert and Elke Knapek / Belgium
- 293 Attenuation of γ -Radiation by Polymer Concrete and Its Resistance to Radioactive Radiation
Surovisev I., Borisov Yu., Perekalsky D. / Russia, Figovsky O. and Bellin D. / Israel
- 299 Hydration Heat and Autogenous Shrinkage of Very-Early Strength Latex Modified Concrete
Pan-Gil Choi, Ki-Kheun Kim, Bong-Hak Lee and Kyong-Ku Yun / Korea
- 309 Photocatalytic Activity of TiO₂ in Polymer Modified Mortar
Elke Knapek, Dionys Van Gemert and Anne Beeldens / Belgium
- 317 Study of Polymer Concrete by Transient Electrochemical Technique
Hongzhu He, Meitun Shi, and Zhiyuan Chen / China
- 321 Development of a Cement-in-Polymer Dispersion for Improved Reinforcement-Matrix Adhesion
Oliver Weichold and Martin Möller / Germany
- 331 Durability Studies on GFRP Rebars
K. Balasubramanian, B. H. Bharathkumar, T. S. Krishnamoorthy, V. Udhayakumar and N. Laxmanan / India
- 341 The Development of Polymer-Based Early Strength Agent
Zhichu Huang, Zhiyin Zhang, Tao Ye and Gaoping Wang / China
- 347 Void and Strength Properties of Porous Polymer Concrete for Pavement with Different Fillers
Young-Ik Kim and Chan-Yong Sung / Korea
- 355 Development of Mix Design for Low-Calcium Fly Ash Based Geo Polymer Concrete
R. Malathy, K. Sasi Kumar and S. Saravanan / India
- 365 Evaluation of Inorganic Polymer As Adhesive Material for Repair of Reinforced Concrete
Fernando Pacheco Torgal, Joao Castro-Gomes and Said Jalali / Portugal
- 373 Durability Performance of Barrier Penetrants on Concrete Surfaces
Haruka Ogawa, Kenji Kano, Toshiyuki Mimura, Kaori Nagai, Atsushi Shirai and Yoshihiko Ohama / Japan
- 383 Reaction to Fire of Polymer-Modified Mortars for Repair Materials for Damaged Reinforced Concrete Structures in Building Construction
Kotabun Yuuki and Yoshihiko Ohama / Japan
- 389 Strength Characteristics of PMMA Mortar Mixed with Reactive Additive
Kyu-Seok Yeon, Jaichul Yi and Hyun-Jong Lee / Korea
- 395 Steel Bar Corrosion in Polymer Concrete with a Bending Crack
Sato Ryuji, Oshima Mitsuharu, Furuta Keichi, Kumieda Minoru and Koyanagi Wataru / Japan
- 403 Study of Polymer Fiber-Reinforced Mortar by Impedance Spectroscopy
Hongzhu He, Meitun Shi, and Zhiyuan Chen / China

- 411 **Effect of Water-Repellent Treatment of Concrete Tested by Migration**
Takehiko Midorikawa and Ichiro Ishikawa / Japan
- 421 **A Study on Using Slag and Steel Fiber to Strengthen the Densification and to Improve the Brittleness of HPC**
Weiming Hou, Jiann-Tsair Chang and Pingkam Chang / China
- 429 **Mechanical Properties of Porous Concrete for Pavement using Recycled Aggregate and Polymer**
Seung-Bum Park, Dae-Seuk Seo and Jun-Lee / Korea
- 441 **Improving the Ductility of usually and High Performance Concrete using the Confinement with Spiral Ties, Steel Fibers and Polymers Fibers**
Naser Kabashi, Cene Krasniqi and Fismik Kadriu / Kosovo
- 451 **Basic Properties of Polymer Concretes using Methyl Methacrylate Solution of Waste EPS**
Hirokatsu Mori, Yutaka Yokoyama and Yoshihiko Ohama / Japan
- 459 **Physical Properties of SBR-Polymer Modified Mortars using Recycled Waste Materials**
Eui-Hwan Hwang, Young-Soo Ko and Jin-Young Shin / Korea
- 469 **Polymercement Materials for Surface Treatment of Concrete with the Utilization of Waste Materials**
Drochytka Rostislav and Nikol Zizkova / Czech Republic
- PART 4 Structural Behavior and Analysis**
- 483 **Flexural Behavior of Latex-Modified Fiber Reinforced Concrete**
Jakob Šušteršič, Andrej Zajc, Vitoslav Dobnikar and Jože Lopatič / Slovenia
- 493 **Structural Behavior of Concrete-Polymer Sheet Interface**
Kuen-Joo Byun, Jin-Won Nam, Ho-Jin Kim and Suk-Hwa Kang / Korea
- 503 **Flexural Behavior of Polymer Concrete Permanent Forms using EPS-MMA-Based Binder**
Bhutta Aamer, Ken Tsuruta and Yoshihiko Ohama / Japan
- 513 **Alternative Ways to Improving the Structural Behavior of Two-Way Slabs with GFRP Bars**
Joo-Ha Lee, Jun-Mo Yang and Young-Soo Yoon / Korea
- 525 **Bond Stresses in Lap-Spliced RC Beams using GFRP Bars: Unconfined Splice Test**
Dong-Uk Choi, Sangsu Ha, and Sungchul Chun / Korea
- 535 **Strengthening of RC Rectangular and T-Beam Strengthened in Flexure and Shear using CFRP**
Asad-ur-Rehman Khan / Malaysia
- 543 **Behaviour of RC Slabs Reinforced with GFRP Rebars under Flexure**
B. H. Bharatkumar, K. Balasubramanian, T. S. Krishnamoorthy, V. Udhayakumar and N. Lakshmanan / India
- PART 5 Development of Protective Coating**
- 553 **How Can We Learn from Customer Complaints?**
A Systematical Approach to Avoid Reclamations from Protective Coatings on Concrete—Peter Seidler / Germany
- 563 **Performance of Protected Concrete against Chemically Aggressive Environments**
Jose Aguiar, Pedro Moreira and Aires Camoes / Portugal
- 573 **Effectiveness of Flexible Polymer-Cement Coatings and Hydrophobic Admixtures against Corrosion of Steel in Reinforced Concrete**
Francesca Tittarelli and Giacomo Moriconi / Italy
- 583 **Blistering of Reactive Polymer Coatings on Concrete, Causes and Prevention**
Lars Wolff, Michael Raupach and Kidist Haitu / Germany
- 595 **Durability of Hydrophobic Agents, used for Chloride Ingress Resistance of Concrete in Marine Environment**
Luc Schueremans, Dionys Van Gemert and Sabine Giessler-Blank / Belgium
- 607 **Basic Properties of Barrier Penetrants as Polymeric Impregnants for Concrete Surfaces**
Atsushi Shirai, Kenji Kano, Kaori Nagai, Kazumao Ide, Haruka Ogawa and Yoshihiko Ohama / Japan
- 617 **Study on Polymer Modified Cement Grouts used in Synchronous Grouting of Shield Tunneling**
Q. J. Ding, K. Tian, H. X. Wang and S. G. Hu / China
- 625 **An Innovative Tensile Bonding Strength Test Method for Repairs: Direct versus Indirect**
Hanfeng Xu and Sidney Mindess / Canada
- PART 6 Application for Pavement and Highways**
- 635 **Investigating the Effect of Concrete Characteristics on Bond Behavior of Latex Modified Concrete Overlays**
Mahmoud Reda Taha / U.S.A. and Kyoung-Kyu Choi / Korea
- 645 **Optimum Rehabilitation of Concrete Bridge Decks on Slovene Motorways using Latex Modified Concrete Overlays**
Marko Lutman and Violeta Bokan Bosiljkov / Slovenia
- 657 **Prediction of Permanent Deformation of Polymer-Modified Asphalt Concretes using Deformation Strength**
Hyun-Hwan Kim, Tae-Won Park, Sung-Hyun Baek, and Kwang-Woo Kim / Korea
- 665 **Estimation of Resistance Against Reflection Cracking of Polymer Modified Concrete**
Jun-Suk Kweon, Byung-Duk Lee, Young-Su Doh and Kwang-Woo Kim / Korea
- 673 **Best Methods for Spall Repair in Concrete Pavements**
David Whitney, David W. Fowler and Dan Zollinger / U.S.A.
- 685 **Fundamental Characteristics of Monomer-Modified Warm-Mix Asphalt Concretes**
Nam-Won Park, Jae-Hyun Jung, Byung-Jin Cho and Kwang-Woo Kim / Korea
- 691 **Influence of Cement on the Breaking of Asphalt Emulsion**
Shuguang Hu, Tao Wang, Fazhou Wang, Zhichao Liu, Tao Gao and Jinzhong Zou / China
- 697 **Fast-Tracking and Sustainability of Very-Early Strength Latex-Modified Concrete in Bridge Deck Overlay**
Sung-Yong Choi, Ki-Heu Kim and Kyoung-Ku Yun / Korea

Volume II

PART 7 Role of Polymers in Rehabilitation

- 707 Concrete Beams and Pipes Bonded by Resin Mortar and Reinforced by FRP Sheets
Makoto Kawakami, Tokushige Hidenobu, Yoshifumi Okayama and Fumitoshi Akimoto / Japan
- 717 Rapid Repair of Damaged Runways using Polymer Concrete
Chul Suh and David W. Fowler / U.S.A
- 725 Investigation and Improvement of Concrete Reinforced with Epoxy Impregnated Fabrics
Ulrich Dilthey, Markus Schleser / Germany and Moshe Putterman / Israel
- 735 Development of a Prototype of Steel Cord Reinforced Polymer as Externally Bonded Reinforcement
Wine Figeys, Luc Schueremans, Dionys Van Gemert and Kris Brosens / Belgium
- 743 The Reinforcement of In Situ Concrete Pressure Pipe with Carbon Fiber Reinforced Polymer (CFRP)
Myles A. Murray / U.S.A.
- 751 Revisiting Ultrasonic Pulse Velocity Measurements as Assessment Method for Polymer-Modified Concrete Patch Repairs
D. Kruger and J.J. Bester / South Africa
- 761 Sprayed FRP for Repairs and Strengthening of Concrete Structures
Seung-Chul Han and Young-Soo Yoon / Korea
- 771 Feasibility Study of Geopolymers for Externally Bonded Reinforcement
Wine Figeys, Dionys Van Gemert / Belgium and José Aguiar / Portugal
- 779 Application of Signal Analysis in Assessment of Repair System Quality by Impact-Echo and Ultrasonic Methods
Tomasz Piotrowski and Andrzej Garbacz / Poland
- 791 Management of Reliability in Concrete Repairs
J.J. Bester and Deon Kruger / South Africa
- 799 Bond Strength and Longevity of Very-Early Strength Latex-Modified Concrete in Concrete Pavement Repairs
Seong-Kwon Kim, Won-Kyong Jeong, Yong-Gon Kim and Kyong-Ku Yun / Korea
- 809 Load Carrying Capacity of Pre-Damaged Reinforced Concrete Beams Repaired with Polymer-Modified Mortar
Abdullah Saad Mohammad, Ismail Salihuddin Radin Sumadi / Malaysia and Musarrat Ullah Khan Afridi / Pakistan
- 817 Deformation Behavior of Repairing-Strengthening Materials with Bonded Epoxy Resins
Cheon-Goo Han, Min-Cheol Han, Hang-Yong Byun, Yong-Kyu Park and Young-Sun Heo / Korea
- 825 The Use of Inorganic Matrix for Bonding Carbon Fiber Sheets to RC Structures
Toutanji Housam and Yong Deng / U.S.A.
- 833 Successful Usage of Prepackaged Polymer-Modified Cementitious Materials In Efficiency Improvement and Rehabilitation of Water-Retaining Structures
Musarrat Ullah Khan Afridi and Abdullah Saad / Malaysia
- 845 An Experimental Study of Macrocell Corrosion of Steel Bars in Reinforced Concrete Structures after Patch Work Using Lightweight Epoxy Mortar and Polymer-Modified Mortar
Shinsuke Kumagai, Hisakazu Horii, Ryutaro Nashimoto, Shinichi Miyazato and Yoshihiko Ohama / Japan

PART 1 Achievements in Concrete-Polymer Composites

- 857 Anticorrosion of Steel by Concrete-Polymer Composites
Yong-Kiug Jo and Wan-Ki Kim / Korea
- 873 Improvement of the Load-Bearing Capacity of Textile Reinforced Concrete by the Use of Polymers
Alessandra Keil and M. Raupach / Germany
- 883 Advances in Adhesion between Polymers and Concrete
Jose Aguiar / Portugal and Dionys Van Gemert / Belgium
- 895 Evaluation of Deflection in Polymer Mortar Sandwich Panels Reinforced with GFRP
Kyu-Seok Yeon, Jaichul Yi and Hyun-Jong Lee / Korea
- 907 NDT-Methods Applicable to Polymer-Cement Composites in the Light of Ohama's Model
Andrzej Garbacz / Poland
- 919 Polymers in Concrete: The Synergistic Effect between Japan and Belgium
Anne Beeldens / Belgium
- 929 Polymer Concretes in South Africa : The Ohama Factor
Deon Kruger / South Africa
- 937 Impact and Influence in India of Dr. Yoshihiko Ohama's Research on Concrete Polymer Composites
Neelamegam M. / India
- PART 2 Celebration**
- 947 Prof. Ohama's Contribution to Concrete-Polymer Composite Research in Korea
Yang-Seob Soh / Korea
- 949 Polymer Concrete and Industrial Floors : Some Considerations on the History of Research with Regard to Protective Coatings on Concrete
Peter Seidler / Germany
- 957 Prof. Ohama and Polymers in Concrete in Japan
Wataru Koyanagi / Japan
- 961 Ohama, a Known Name in the Area of Concrete-Polymer Composites in China
Zhiyuan Chen and Shiyun Zhong / China
- 965 My Friend Yoshi
David W. Fowler / U.S.A.
- 969 The Past, Present and Future of Concrete-Polymer Composites : A Life's Work
Yoshihiko Ohama / Japan

6 CONCLUSIONS

1. The developed mix proportion for M20 grade to M40 grade Geo Polymer concrete is attaining the target strength
2. Geo Polymer Concrete is achieving higher strength at early stage when compare to normal concrete.
3. Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of fly ash-based geopolymer concrete.
4. Higher the ratio of sodium silicate-to-sodium hydroxide ratio by mass, higher is the compressive strength of fly ash-based geopolymer concrete.
5. Curing time, in the range of 2 days, produces higher compressive strength of fly ash-based geopolymer concrete however; the increase in strength beyond 7 days is not significant.
6. The slump value of the fresh fly-ash-based geopolymer concrete increases with the increase of extra water added to the mixture.
7. The Rest Period, defined as the time taken between casting of specimens and the commencement of curing, of up to 5 days increases the compressive strength of hardened fly ash-based geopolymer concrete. The increase in strength is substantial in the first 3 days of Rest Period.
8. The fresh fly ash-based geopolymer concrete is easily handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength.
9. As the H₂O-to-Na₂O molar ratio increases, the compressive strength of fly ash-based geopolymer concrete decreases.
10. As the ratio of water-to-geopolymer solids by mass increases, the Compressive strength of fly ash-based geopolymer concrete decreases.
11. The average density of fly ash-based geopolymer concrete is similar to that of OPC concrete.

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Evaluation of Inorganic Polymer as Adhesive Material for Repair of Reinforced Concrete

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ABSTRACT

A new development in the repair and strengthening of reinforced concrete systems is the use of carbon fiber reinforced polymers (CFRP) strips bonded to concrete substrate with epoxy resins. It has been reported that epoxy adhesive used are extremely sensitive to high temperatures. Some authors conclude that the epoxy temperature should not exceed 70 °C in order to safeguard the adhesiveness of the epoxy and, thus, the integrity and adequate functioning of CFRP. It is noted that frequently exposure to direct sunlight causes temperatures higher than 70 °C. Inorganic polymers are often referred to as geopolymers or alkali-activated cements and are known to possess high stability at high temperature. Tungsten mine waste inorganic polymer (TMWIP) is a new cementitious material, obtained from dehydroxylated mine waste powder mixed with minor quantities of calcium hydroxide and activated by NaOH and water/glass solutions. This paper reports some results on the bonding capacity of this inorganic polymer, i.e. TMWIP, and concrete. Results show that given the proper mix the new binder demonstrates high adhesion to concrete substrate.

KEYWORDS: reinforced concrete, inorganic polymers, repair material, elasticity, mine waste

1 INTRODUCTION

A new development in the repair and strengthening of reinforced concrete systems is the use of carbon fiber reinforced polymers (CFRP) strips bonded to concrete substrate with epoxy resins. This method is a relatively new retrofitting method, developed first in Japan [1,2]. Epoxy adhesive being used in the construction industry is very sensitive to temperature variations. Both experimental and finite element results show that the epoxy temperature should not exceed 70 °C in order to maintain the integrity between the CFRP and concrete [3]. It is noted that frequently exposure to direct sunlight causes temperatures higher than 70 °C which causes malfunction CFRP. This means that adhesive materials that remain stable with higher temperatures are needed. Inorganic polymers are often referred to as geopolymers or alkali-activated cements and are known to possess high stability at high temperature. Studies of alkali-activated cements

have a long history in the former Soviet Union, Scandinavia, and Eastern Europe [4]. In 1978, Davidovits created the term "geopolymer", to characterise new materials with the ability to transform, polycondense and adopt a shape rapidly at low temperatures like "polymers" [5]. The polymerisation process involves a chemical reaction under highly alkaline conditions on Al-Si minerals yielding polymeric Si-O-Al-O bonds with empirical formula $Mn [-(Si-O)_2z-Al-O]n \cdot nH_2O$, where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium [6]. Davidovits reported several advantages of geopolymeric cementitious systems over Portland cement mainly environmental, due to the fact that geopolymeric based concrete has a much longer service life than Portland cement based ones, to the metals waste encapsulation capacity and to lower CO₂ emissions [7]. The geopolymerization requires a precursor that contains significant quantities of silicon and aluminium held in an amorphous phase such as ashes from power stations or mining and quarrying wastes.

Over the last years several authors have reported research in a large number of aspects related to geopolymeric based binders such as: dependence of the nature on source materials (geopolymers synthesised from calcined sources show a higher compressive strength than from raw materials) [8,9], immobilization of toxic metals [10-12], reaction mechanisms and hydration products [13-17], the role of calcium in geopolymerization [18-21], manufacture operations [22,23] and even the development of lightweight building materials [24]. Tungsten mine waste inorganic polymer (TMWIP) is a new cementitious material, obtained from dehydroxylated mine waste powder mixed with minor quantities of calcium hydroxide and activated by NaOH and waterglass solutions. This paper reports some results on the bonding capacity of this inorganic polymer, i.e. TMWIP, and concrete.

2 EXPERIMENTAL PROGRAM

2.1 Materials

2.1.1 TMWIP geopolymeric binder

The TMWIP geopolymeric binder used in this investigation as repair product was made using tungsten mine waste mud previously subject to a thermal treatment at 950° C during 2 hours, in order to achieve the dehydroxylated state. Mineralogical composition and thermal conditions have been described elsewhere [27]. The chemical composition of the mine waste mud is shown in Table 1.

Table 1. Gradation and physical characteristics of aggregates

	Cumulative percentage retained	
	Fine aggregate	Coarse aggregate
9,5mm	0	0
4,76mm	0	35,4
2,38mm	0	91,5
1,19mm	13,9	97,2
590µm	61,6	98,5
297µm	97,3	99,2
149µm	99,7	99,4
74µm	99,9	99,6
Dust content (<74µm)	0	0,4
Fineness modulus	2,72	5,2
Max. dimension (mm)	2,38	9,52
Water absorption (%)	0,	0,4
Density (Kg/m ³)	2624	2689

2.1.2 OPC concrete substrate

The properties of the aggregates used to make the concrete substrates are shown in table 2. Using the Faury concrete mix design method [25], a C30/37 strength class concrete was designed. The concrete mixes and their main properties are described in Table 3. The concrete specimens were cured immersed in water during 3 months. This curing period provides an almost as complete concrete hydration as old concretes in field practice and has been used by other authors [26].

Table 2. Mix proportions and main properties of the concrete substrates

Components	C30/37
Cement II 32,5 (Kg/m ³)	504
Fine river sand	417
Coarse aggregate	1154
W/C ratio	0,43
fc _{28d} ^a (MPa)	37,8
f _{t28d} ^b (MPa)	8,7

[Note] ^aAverage value of three specimens (150×150×150mm³), ^bAverage value of six specimens (40×40×160mm³)

Table 1. Chemical composition of TMWIP (%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	S O ₄	Ti O ₂	As	Other minor oxides
53,48	16,66	12,33	7,65	0,62	1,27	3,10	1,39	1,28	2,22

The SiO₂/Al₂O₃ atomic ratio is 5,5 higher than the one suggested by Davidovits of about 2 for making cement and concrete, however the final SiO₂/Al₂O₃ atomic ratio in the hardened binder depends mainly on the reactivity of Al-Si because not all the silica and alumina are reactive so even despite the fact Al and Si have synchro-dissolution behaviour in alkaline solution, meaning they dissolve from the mineral in some linked form one cannot expect the same Si/Al ratio in the final hydration product as the one present in the original precursor material. Indeed most of the Al-Si materials cannot even supply sufficient Si in alkaline solution to start geopolymerization, this explains why they need extra silica provided in solution by waterglass, which influences the Si/Al ratio of the hardened binder.

The XRD patterns indicated that mine waste mud consists mainly of muscovite and quartz which were identified by their characteristic patterns as follows: muscovite (card 46 - 1409) and quartz (card 46 - 1045). For those thermal conditions XRD patterns indicated that dehydroxylation did not result in a complete collapse of muscovite structure. Calcination leads to formation of an amorphous phase, causing an increase in the general background (BG) of XRD patterns and dominantly taking place in the calcinations interval from 850 to 950° C, with a thermal behaviour similar to other phyllosilicate clay minerals. The main muscovite peak (2θ=8,8°) persisted even after the sample had been heated at 950° C although it decreased considerably. Peak area measurements revealed that about 12% of muscovite survived calcination at 950° C. Molecular changes during dehydroxylation were also examined with infrared emission spectra (FTIR), confirming decrease in the absorption peaks at 3600-3700 (OH stretch), however the main muscovite peak did not disappear totally indicating only a partial transformation.

The geopolymeric binder used was a mixture of coarse aggregates, mine waste mud, calcium hydroxide, alkaline silicate solution and water. The coarse aggregates were the same used in the design of concrete substrate. The mass ratio of coarse aggregates, waste mud: and alkaline activator was 1,5:1:1. Calcium hydroxide was used to replace mine waste mud with a percentage substitution of 10%, because this percentage has been found to lead to the highest compressive strengths [28]. An activator with sodium

hydroxide (24M) and sodium silicate solution ($\text{Na}_2\text{O}=8.6\%$, $\text{SiO}_2=27.8\%$, $\text{Al}_2\text{O}_3=0.4\%$ and water=63.2%) was used with a mass ratio of 1:2.5. Previous investigations have shown that these conditions lead to the highest long term compressive strength results in alkali-activated TMWM binders [29]. Distilled water was used to dissolve the sodium hydroxide flakes to avoid the effect of unknown contaminants in the mixing water. The alkaline activator was prepared prior to use. The sand, mine waste mud and calcium hydroxide were dry mixed before being added to the activator. The compressive and tensile strength of geopolymeric based binder was as follows:

$$f_{c,1d} = 47\text{MPa}, f_{c,7d} = 60.3\text{MPa}, f_{c,14d} = 71\text{MPa}, f_{c,28d} = 78.3\text{MPa}$$

$$f_{t,1d} = 7\text{MPa}, f_{t,7d} = 11.5\text{MPa}, f_{t,14d} = 13.6\text{MPa}, f_{t,28d} = 10.7\text{MPa}$$

2.2 Specimen preparation, bond strength testing and microanalysis

Bond strength was assessed from a slant shear test. The slant shear test uses square prisms made of two halves, one of the concrete substrate and one of the repair material, tested under axial compression. The adopted geometry for the slant shear specimens was a $50 \times 50 \times 125\text{mm}^3$ prism with an interface line at 30° to the vertical (Figure 1). Bond strength was calculated by dividing the maximum load at failure by the bond area and was obtained from an average of 4 specimens determined at the ages of 1, 3, 7, and 28 days of curing.

In order to increase the specific surface of the concrete substrate an etching procedure was carried out. The concrete surface was immersed in a 5% hydrochloric acid solution for 5 minutes and then carefully washed to ensure the removal of CaCl_2 which results from the reaction between HCl and $\text{Ca}(\text{OH})_2$. According to some researchers this procedure leads to an increase of micro and fine roughness of the concrete substrate [30].

The specimens were named after the repair materials and concrete substrate surface treatments. Specimens using concrete substrate repaired TMWIP geopolymer with and with no surface treatment were named respectively, GP - ES (Etched surface) and GP - NTS (No treatment surface). Slant specimens with substrate surface treatment as cast against metallic formwork, and as cast against wood formwork were also used repaired with TMWM geopolymeric binder and were named, GP-MF and GP-WF respectively. For examination by scanning electron microscopy (SEM), the specimens were embedded into a low viscosity epoxy resin, cut and polished. After the lapping stage an additional epoxy impregnation was performed, and the samples were relapped in order to ensure full resin impregnation and a good quality polish. The samples were then carbon-coated. A Hitachi S2700 scanning electron microscope was used equipped with a solid backscattered detector.

3 RESULTS AND DISCUSSION

The results of the effect of the several repair solutions on average bond strength are shown in Figure 3. The failure modes were characterized by the location of the failure in the slant specimens. An adhesive failure occurs when the plane of failure is along the interface surface (Figure 4a). Figure 4b shows a slant specimen failed in a monolithic failure mode. The values of bond strength in slant specimens with a monolithic failure mode are a lower estimate. It can be seen that the specimens repaired with the TMIP geopolymeric binder present the high bond strength's even at early ages. Specimens repaired with geopolymeric binder with 1 day curing have higher bond strength than specimens repaired with current commercial products after 28 days curing. Specimens repaired with the TMIP geopolymeric binder appear to be influenced not by the chemical treatment in sawn concrete surface substrates, but by the use of concrete surfaces as cast against formwork. Those kinds of surfaces are rich in calcium hydroxide but lack exposed coarse aggregates which could contribute to improve bond strength due to silica dissolution from the aggregate surface. This is consistent with previous research by the authors [29].

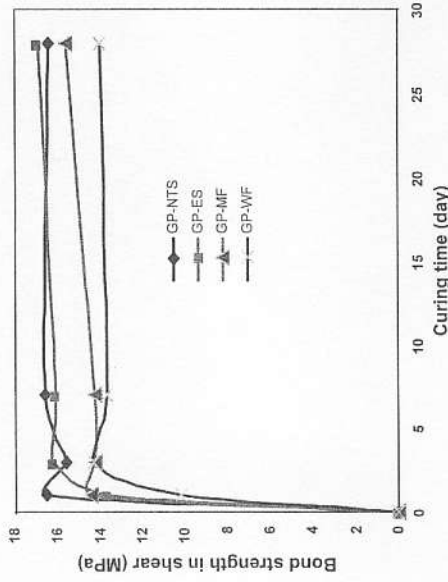


Figure 3. Slant shear test results.

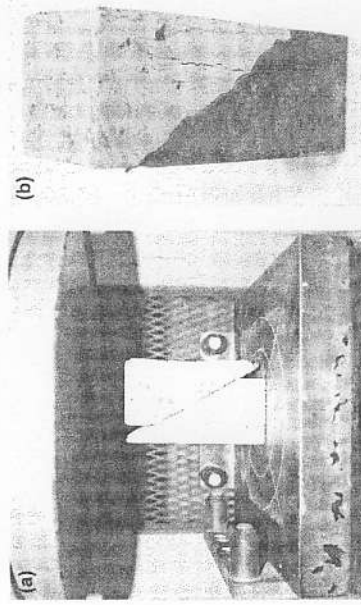


Figure 4. Slant specimens failure mode; (a) Adhesive failure and (b) Monolithic failure.

Table 4 shows the number of specimens that had an adhesive failure. As can be seen, only the slant specimens repaired with the geopolymeric binder and saw concrete substrates present monolithic failures due to its high bond strength.

Table 4. Specimens with an adhesive failure

	Concrete surface treatment			
	ES	NTS	MF	WF
Curing days	1	2	0	4
	3	0	0	4
	7	0	0	4
	28	0	0	4

Table 5 shows the coefficient of variation (COV) of bond strengths according to curing age. The results show that in all cases, COV decreases with curing age and shear strength increases except in the case of the specimens repaired with the TMWM geopolymetric binder and with chemical surface treatment (GP-ES). The specimens repaired with the TMWM geopolymetric binder show low COV values even at early ages and are not influenced by the chemical treatment.

Table 5. Coefficient of variation of bond strength (%)

	Concrete surface treatment			
	ES	NTS	MF	WF
Curing days	1	6,7	12,5	14,8
	3	5,6	8,4	6,3
	7	5,6	6,0	7,7
	28	6,0	6,1	7,0
				1,4

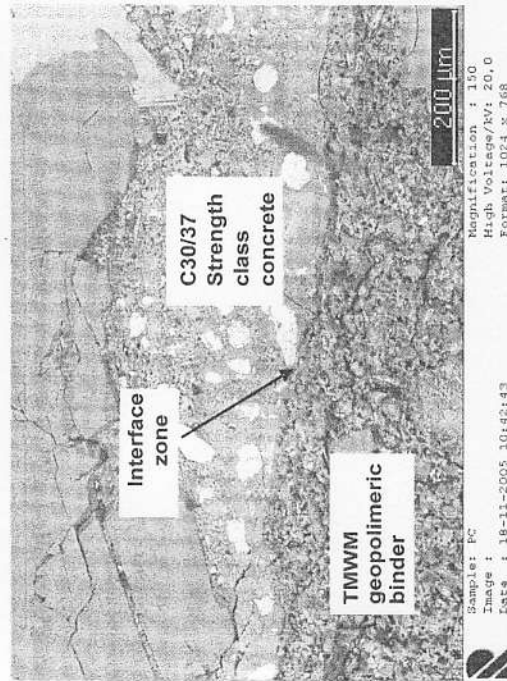


Figure 5. SEM micrographs of interfacial transition zone between concrete substrate and geopolymetric binder.

The explanation for this behaviour lies in the fact that OPC concrete substrate surfaces are rich in calcium hydroxide, that reacts to geopolymetric based binders due to the need for positive ions such as Ca^{++} to be present in the framework cavities to balance the negative charge of Al^{3-} ions and also to the mechanical interlock yield by silica dissolution from aggregate surface when subject to the high alkaline activator. Thus, the concrete substrate chemically bonds to the geopolymetric phase, as it can be seen by the absence of a clear interfacial transition zone on a microstructural level (see Figure 5).

4 CONCLUSIONS

The following conclusions can be drawn from this study:

TMWIP geopolymetric binder present high bond strength even at early ages (just after the first day). Furthermore bond strength is not affected by low roughness surface treatment of concrete substrate. Since bond strength is still very high for concrete substrate specimens as cast against metallic formwork which represents the majority of concrete structures surfaces it means TMWIP could be used to replace epoxy resins when CFRP strips are used in retrofitting operations.

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Durability Performance of Barrier Penetrants on Concrete Surfaces

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ABSTRACT

Various barrier penetrants have been used to improve the durability and to prevent the fouling of fair-faced concrete. However, there have been insufficient studies on their durability. This paper describes the results of durability tests (accelerated carbonation, chloride ion penetration, freeze-thaw and accelerated weathering) on the mortars coated with major commercial silane-, acrylic-resin- and silicate-based barrier penetrants used in Japan. The following conclusions were reached. (i) Coating with barrier penetrants can improve the resistance to carbonation and chloride ion penetration of mortar. However, the effects depend on the main ingredient of the barrier penetrants. (ii) Coating with barrier penetrants can improve the freeze-thaw durability of mortar. However, the effect of the main ingredient of the barrier penetrants on freeze-thaw durability is unclear. (iii) The effect on the water absorption reduction of mortar after accelerated weathering depends greatly on the main ingredient of the barrier penetrants. (iv) Coating with barrier penetrants can improve the durability of mortar. However, the effect depends greatly on the main ingredient of the barrier penetrants.

KEYWORDS: barrier penetrants, concrete, carbonation resistance, chloride ion penetration resistance, freeze-thaw durability, weatherability

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