

Mining and agricultural Residues-based composites materials for engineering applications: Red mud and Rice husk Ash Geopolymers

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Abstract: The processing of raw materials into finite products releases residues and waste, the management of which becomes an environmental matter. In the Bayer process the reaction of bauxite mineral with NaOH for alumina production releases red mud RM, a waste that occupies land and causes environmental hazards. Rice is the staple food for a large part of the population in Guinea. Rice husk RH is generated in bulk quantities and poses environmental hazards. It contains approximately 20% silica a suitable material for a wide range of application. After burning the resulting rice husk ash RHA contains about 90% silica.

Geopolymer technology is a promising application for the use of industrial wastes. For the synthesis of a RM/RHA based composite Geopolymer (GP), RM from a local Alumina Plant; RH from a local mill in Guinea and water glass solution WGS were used. Different mix ratios of RM, RHA and WGS were performed. The specimens were tested for compressive strength at different temperatures. X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) were used to investigate the microstructure of parent materials and the resulting GP specimens. The analyses showed that the final product is mainly composed of amorphous Geopolymer material and that higher temperatures improve the compressive strength.

Key words: red mud, rice husk, geopolymer, material, silicate

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I. Introduction

Guinea is referred to as geological scandal because of the prominence and the variety of its mineral resources. Several studies concede that the country is home to 33% of the world's known bauxite reserves. Red mud is a reddish-brown solid waste resulting from the digestion of bauxite ores with caustic soda for alumina production. The issue of managing the RM rose with the process developed by J. Karl Bayer for alumina refining and the recognition that it generated a large amount of waste material.

Human activities inevitably result in wastes, The higher the material turnover, and the more complex and divers the materials produced, the more challenging it is for waste management to reach the goals of "protection of men and environment" and "resource conservation [1] The huge amount of industrial byproduct, residue and waste continue to pose a great challenge with regard to their disposal due to the environmental, health, lands and other issues, It is recognized that the best approach in overcoming the aforementioned waste management issue is to promote recycling or reuse. Nowadays, the rapid growth in research and development related to geopolymer composites has indicated that the use of geopolymer composite offers a great potential in solving not only the waste management problems but also the environmental degradation related to the use of primary binder material in the construction industry [2]. Composite materials typically consist of two or more components that comprise significantly different physical and/or chemical properties. Due to the controlled combination of the components, new materials are obtained with distinct properties from the individual components [3]. Composite materials are dedicated to be employed instead of traditional materials due to their enhanced materials performance involving high strength, toughness, heat resistance, light weight, impermeability against gasses, thermal endurance and stability in the presence of aggressive chemicals, water and hydrocarbons, high resistance to fatigue and corrosion degradation, re-processing recyclability and less leakage of small molecules such as stabilizers, etc. [4].

RM

Various types of bauxite differ considerably with regard to extraction yields of available alumina. The chemical treatment of bauxite with caustic soda to produce alumina is known as the Bayer process, The residue resulting from this process is known as red mud with a pH about 11, Generally evacuated and disposed in huge landfills [5]. The amount of bauxite needed to produce one ton of alumina and, thus, the resulting amount of red mud varies

considerably for each deposit, This is an expression of the highly heterogeneous site-specific chemical and mineralogical characteristics of bauxite ores. [6].

Red mud is the major waste material produced during alumina production following the Bayer process, Depending on the quality of the raw material processed, it was reported that 0,8~1,5 t of red mud is produced by each 1 t alumina produced, Globally, the total amount of red mud produced every year is between 60 and 120 million tons [7].

The impact of RM on the environment is diverse [8] : contamination of surface and underground water resources with NaOH and metallic oxide-bearing impurities; direct contact with fauna and flora; evaporation that could originate highly alkaline rainfalls,

Due to the properties of fine particles, the high alkalinity and other metal content, the disposal of RM is a serious environmental concern comprising soil contamination, groundwater pollution and fine particles' suspension in the sea. Moreover, the storage of red mud in lakes or ponds occupies huge areas of land ; dry RM leads to health problem. Many recent studies and semi-industrial trials were directed to the incorporation of the red mud in construction materials; traditional ceramics clinker; light weight aggregates.

RH and RHA

Rice is probably the second largest produced cereal in the world, Its production is geographically concentrated in Asia. Since decades rice becomes the basic food for the great majority of the population in Guinea. Therefore the government implements several initiatives in order to increase rice production with the aim of reducing dependance on import. Amongst the variety of biomasses available, RH occupies a preeminent position, not only in terms of its amount produced worldwide, but also because of its unique chemistry-related features. Rice plants absorb water-soluble siliceous ions via their root. The ions are transported to stems, leaves and RH by sap flow, In RH, siliceous ions accumulate at the cuticle outside of the epidermis [9].

Due to its high silicon content, RH has become a source for preparation of elementary silicon and a number of silicon compounds especially silica [10], silicon carbide, RHA is rich in silica about 60-90% and varies from gray to black depending on inorganic impurities and un-burned carbon amounts [11]. The silica content in the RHA varies from 90 to 95 wt.%, which exists predominantly in an amorphous phase and partly in a crystalline phase [12].

Geopolymer Chemistry

Geopolymer is essentially a chemical compound mineral or a mixture of compounds consisting of units, for example silico-oxide (—Si—O—Si—O—), silico-aluminate (—Si—O—Al—O—), ferro-silico-aluminate (—Fe—O—Si—O—Al—O—) or alumino-phosphate (—Al—O—P—O—), resulting from a geopolymerization process. The technology allows the manufacture of materials used in ceramic applications, high-tech fibrous composites for the automotive, aeronautics and defense industries, fire-resistant paints and glues without organic solvent, among others. The process allows also the production of biomaterials for bone prostheses, and new ecological cements without CO₂ greenhouse gas emissions.

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material generically called a 'geopolymer', after Davidovits [13]. Geopolymers can be produced from a range of aluminate and silicate materials including RHA, metakaolin, fly ash, blast furnace slags, and mineral processing wastes As such, most industrial precincts would produce a range of suitable feedstock to enable geopolymer production [14].

Geopolymers are currently developed and applied in nine main classes of materials characterized by the Si:Al atomic ratio:

- Si:Al = 1:0, silicate-based geopolymer, poly(siloxonate), soluble alkali silicate;
- Si:Al = 1:1, geopolymer based on kaolinite/hydrosodalite, poly(sialate);
- Si:Al = 2:1, geopolymer based on metakaolin MK-750, poly(sialate-siloxo);
- Si:Al = 1, 2, 3, geopolymer based on silicoaluminate calcium (blast furnace slag), (Ca,K,Na)-poly(sialate);
- Si:Al = 2:1, geopolymer based on fly ash from coal-fired thermal power plant, crosslinking (Ca, K, Na)-poly(sialate-siloxo);
- $1 < \text{Si:Al} < 5$, rock-based geopolymer, poly(sialatemultisiloxo);
- $5 < \text{Si:Al} < 35$, silica-based geopolymer, crosslinking sialate and siloxo in a poly(siloxonate); as well as
- AlPO₄ type phosphate-based geopolymer;
- geopolymer based on organo-mineral (epoxy-sialate) [15].

The use of multiple and varied feedstock in geopolymer production has led to a focus on understanding the chemistry of the amorphous reactive components. This in turn allows geopolymer products to be formulated with predictable performance properties [16]. The geopolymerization mechanism involves Si and Al dissolution from the starting materials generates to make available polysialate units. The term poly(sialate) has been proposed to designate geopolymers sodium, potassium and calcium silicoaluminates [17].The sialate network is made up of

groups (SiO) connected by covalent bond Si—O—Al—. The cations (Na, H₃O⁺) present in the structural cavities of the poly(sialate) balance the negative charge of Al³⁺ in coordination (IV). The empirical formula for polysialates is: 4) and (AlO⁺, K⁺, Ca⁴⁺⁺

with M representing the cation K, Na or Ca,

n degree of polymerization,

z equal to 1, 2, 3 or more, up to 32,

w number of water molecules.

The first three geopolymers are of the type:

– poly(sialate)

Mn-(—Si—O—Al—O—) *M-PS* Si: Al = 1:1

– poly(sialate-siloxo)

Mn-(Si—O—Al—O—Si—O—)_{*n*} *M-PSS* Si: Al = 2:1

– poly(sialate-disiloxo)

Mn-(Si—O—Al—O—Si—O—Si—O—)_{*n*} *M-PSDS* Si: Al = 3:1

II. Material And Methods

The RM slurry with an alkaline pH 11 was sourced from the Alumina Plant in Fria. It was dried at the temperature of 50°C during 72 h and cooled at ambient temperature. A porcelain mortar was used to break down the RM aggregates, and to pulverize it to a powder with fine particles about 250 mm sieves. The raw RH was collected from a local rice mill at Dinguraye. It was burned at 700°C for 1 hour. The resulting RHA was ground for 30 minutes, passed through 90 mm-mesh. As alkaline sodium silicate solution or water glass (Merck ; Germany) containing Na₂O 10.6wt%, SiO₂ 26.5 wt. %, H₂O were used. For subsequent mechanical and microstructural tests, the geopolymer mixtures were grouped into three, namely GPA ; GPB and GPC. The preparation consisted of mixing the two dry RM and RHA powders after the scheme in table below.

Table 1 : Mix proportions for the GP synthesis

Samples	Specimen	Materials mix ratio		
		RM	RHA	WGS
GPA	GPA1	20	65	15
	GPA2	40	45	15
	GPA3	60	35	15
GPB	GPB1	25	60	15
	GPB2	45	40	15
	GPB3	65	20	15
GPC	GPC1	30	55	15
	GPC2	55	30	15
	GPC3	70	15	15

For reproducibility of GP morphology and properties, 3 specimens for each sample were performed. The mixing of the blends was carried out by Heidolph ST-1 Laboratory magnetic stirrer at two different speeds ; 100 rpm for 5 min and 200 rpm for 15 min, to insure their homogeneity. Then the water glass solution was added to the RM/RHA powder. The specimens of the resulting GP precursor were poured in 50x50x50 mm³ molds. They were then demolded and subjected to curing in a laboratory ambient during 28 days. Some specimens were subjected to heat resistance test at 1000°C.

The microstructure of parent materials RHA, RM and the synthesized GP geopolymer specimens were characterized by X-ray diffraction (Rigaku Geigerflex D/max– Series instrument) and by Scanning Electron Micrograph (SEM– Hitachi, SU 70). Specimen with the highest compressive strength and heat resistance was subject to microstructure characterization. The compressive strength tests were performed on the mix specimens on a Shimadzu apparatus (Model: AG-X/R Refresh).

III. Results And Discussion

The mineralogical composition of RM and RHA are listed in Table 2. RM is largely composed of a high hematite and alumina content : 55,89 and 14,68% respectively. While the major constituents of RHA are amorphous silica SiO₂ 89,75%. It is known that the amorphous constituents are necessary conditions to conduct geopolymerization for RM based geopolymer materials. Therefore RM and RHA composition with regard to Si content, are suitable reactants in this study.

Table 2 :Mineral composition of parent materials (%)

Minerals	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	P ₂ O ₅	CO ₂	Total
RM	7,06	14,68	55,89	2,1	0,25	0,06	3,12	1,21	14,6	98,97
RHA	88,75	1,93	1,03	1,41	0,2	1,73	-	1,87	-	97,46

RM and RHA Micromorphology

Understanding the micromorphology of the RM and RHA contributes to identify whether some phases such as nonreactive or unreacted reactive phases in the final products are inherited from the parent materials. Fig.1 shows the micrograph features of the two raw materials.

The RM is characterized by irregularly shaped aggregates that appear to be porous and comprised of much smaller particles (Fig.1/a). Thus the aggregates are most likely hematite particles. The regular RHA particles are much more variable in size and most of them have a thin shell or plate like shape.

In the SEM micrograph of RM it is observed that the arrangement of the particles is relatively loose with high porosity and small particle size. It is characterized by irregularly shaped aggregates that appear to be porous and comprised of much smaller particles (Fig.1/a). Thus the aggregates are most likely hematite particles.

The morphological features in the SEM micrograph of RHA exhibits a porous and multifaceted particle shape and size (Fig.1/b). The regular RHA particles are much more variable in size and most of them have a thin shell or plate like shape.

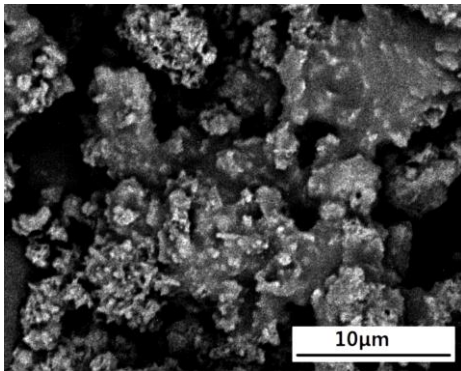


Fig.1/a: The SEM micrograph of RM

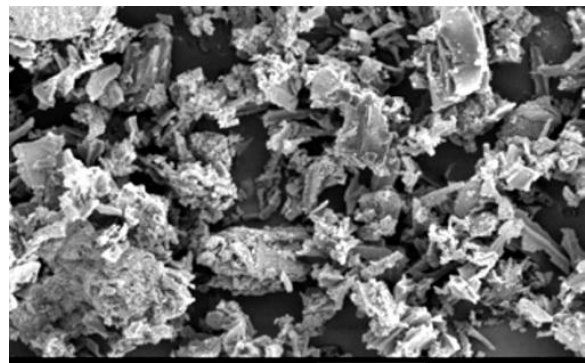


Fig.1/b: SEM micrograph of RHA

In the RHA porous and honeycomb morphology are observed and can be attributed to the burning out of the organic component in the source RH during combustion. The hydrated silica subsequently polymerizes to form a skeletal silica network which may explain the flaky and honey comb-like structure in the micrograph.

RM has relatively movable and porous microstructure with the presence of dispersive particles. Moreover, the diagram shows unequal formed aggregates comprising smaller particles. The aggregates are probably hematite particles and needle-shaped particles of gypsum.

XRD diffraction Analysis

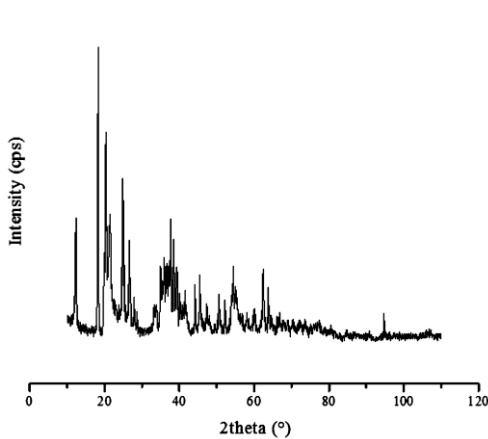


Fig.2/a: XRD of RM

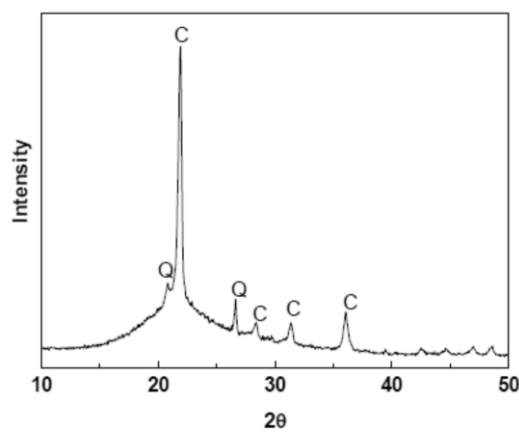


Fig.2/b: XRD of RHA (C : cristobalite; Q : quartz)

Fig.2 shows the XRD patterns of the parent materials RM, RHA. As shown from the XRD of RM, evidence of amorphous was observed. Some sharp peaks associated with crystalline minerals of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) at 18° and iron oxide (Fe_2O_3) at 20° in XRD pattern of RM. The XRD of RM is characterized by the presence of sharp peaks mainly caused by the presence of hematite Fe_2O_3 , gibbsite $\text{Al}(\text{OH})_3$, akdalaite

$4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, lepidocrocite $\text{FeO}(\text{OH})$ and calcite CaCO_3 . There is no broad humps in the pattern hence the amorphous phases are not present at large quantities. RM contains Al_2O_3 as indicated in Table 2 but no alumina peaks are identified suggesting that the alumina in the RM mainly presents as an amorphous phase. Therefore RM provides no NaOH and Al in the geopolymerization process, but little Si.

RHA diagram shows a very high content of silicon over 90% and a relative low presence of Al_2O_3 and Fe_2O_3 . In the RHA, Na_2O amount is insignificant. It indicates that RHA is formed by silica in the crystalline form, resulting from the predominant presence of cristobalite ($2\theta = 21.9$) [18].

The XRD pattern of RHA shows a sharp peak resulting probably from cristobalite superimposed on a broad hump from amorphous silica, at $10\text{--}35^\circ 2\theta$. [19]. According to its chemical composition, silica in the RHA is mainly present as amorphous phase with cristobalite [20]. RHA contained mainly stable crystals of cristobalite and the SEM image of the RHA particles were irregular in shape. One weaker peak produce by quartz is present but not quiet visible due to the hump from the amorphous silica and trace crystalline of quartz has also been observed.

SEM and XRD of GP

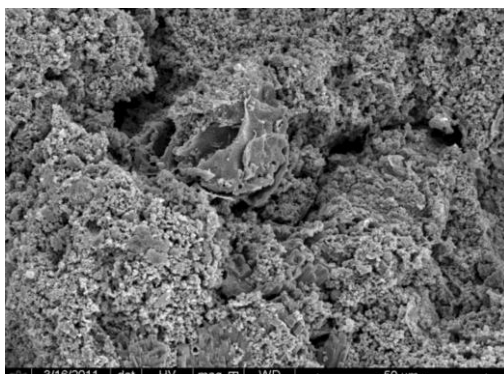


Fig.3: SEM observation of GPB1

The microstructure of a representative fractured surface from a GPB geopolymer specimen, shows porous and inhomogeneous microstructure with microcracks and microvoids. The SEM shows that the microstructure of RHA and RM geopolymer comprises non-dissolved particles of RM, which are bonded in an extent gel phase and the formation of gel silicate (Fig.3). The reaction with the alkaline solution to form a particulate gel network took place at the border of particles then involving the entire surface. Several studies claim that the solid to liquid (S/L) ratio and the sodium hydroxide and silicon concentrations in the aqueous phase are the main synthesis parameters affecting the physical and mechanical properties of geopolymers [21].

XRD of GP Geopolymer

The XRD pattern of GPB specimen shows that main compositions in the crystalline structure of GP materials are silicon oxide (at $22^\circ 2\theta$ angle) and some minerals such as sodium aluminum silicate (at $21.5^\circ 2\theta$), iron silicon oxide ($36^\circ 2\theta$ angle). Two peaks of gibbsite and iron oxide at $18^\circ 2\theta$ and $20^\circ 2\theta$, respectively are typically associated with red mud raw material (Fig. 1a) disappeared in this XRD spectrum because there was reaction of geopolymerization among reactants resulting to an increase of mechanical strength of geopolymer specimens.

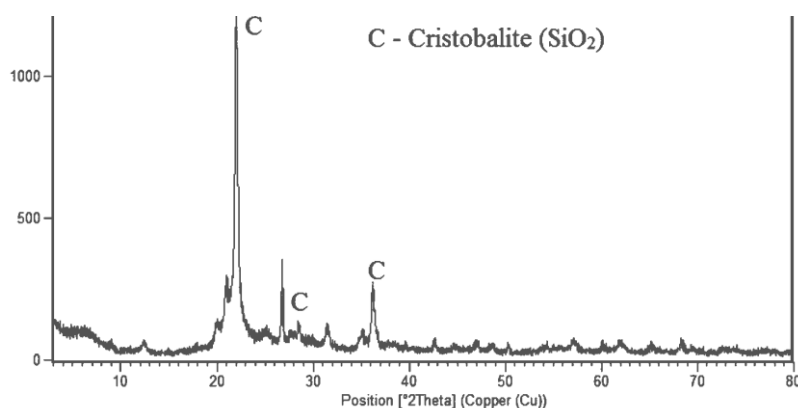
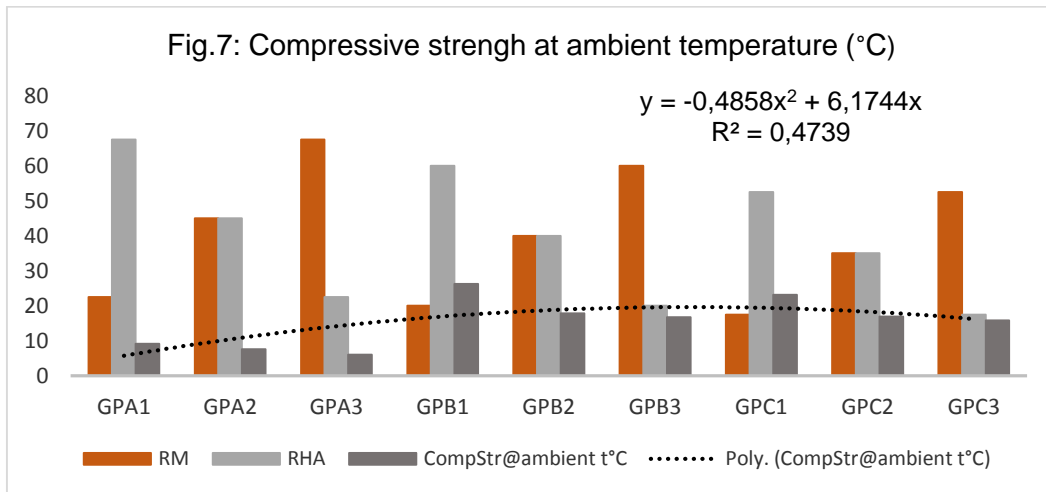


Fig.3: XRD Pattern of GPB1

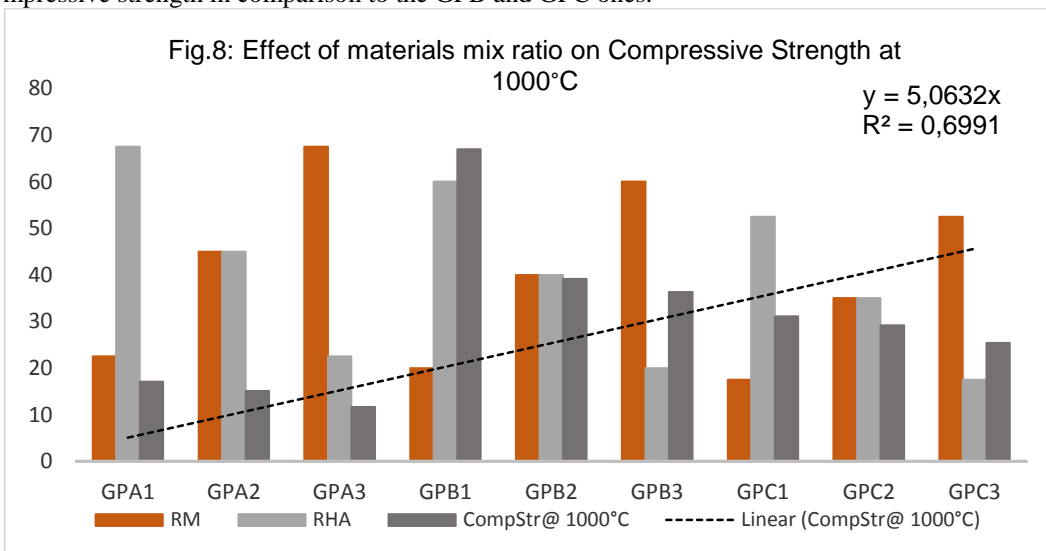
The XRD diagram of GPB1 specimen shows that the product is not clean geopolymer matrix, but a composite consisting of the geopolymer structure and crystalline phases from parent materials. It is certainly a composite containing two solid parts, explicitly the non-dissolved solid particles and the formed geopolymeric binder. The XRD patterns show a broad reflection related to the high amorphous content. However, the center of this reflection is shifted to $2\theta = 29^\circ$ due to changes in composition and structure when RHA is activated by NaOH and NaSiO₂ solutions. The specimen shows that the product is not clean geopolymer matrix, but a composite consisting of the geopolymer structure and crystalline phases from parent materials [22].

The main compositions in the crystalline structure are silicon oxide, cristobalite (at 22° - 2θ angle) and some minerals such as sodium aluminum silicate (at 21.5° - 2θ), iron silicon oxide (36° - 2θ angle). Amorphous phase in the microstructure of GP geopolymer

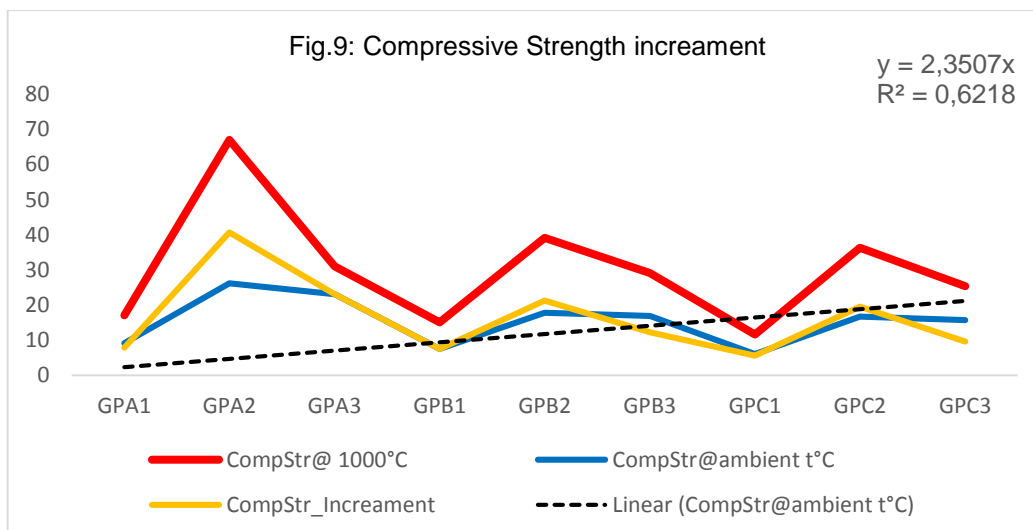
Compressive strength test



Both at room temperature and at 1000°C the GPB combination develops the highest compressive strength and the GPC combination shows the lowest compressive strength. At ambient temperature in GPA combination exhibits low compressive strength in comparison to the GPB and GPC ones.



The greatest value of compressive strength was developed by the GPB1 specimen exhibited a strength : 36,31 MPa at ambient temperature and 66,97 Mpa at 1000°C. The heating process results with significantly increase of the compressive strength of about 250%. This is probably due to sintering that may be occurred at high temperature in geopolymer samples, similar to what is happening in ceramic process [23], [24].



IV. Conclusion

The transformation of the huge mineral resources into finite products will lead to the of equivalent amounts of residues. In order to reduce the adverse impact of waste on the environment and occupation of land resources the waste management becomes an environmental and health issue. Red mud and rice husk resulting from the alumina production and rice mills respectively, are typical cases. The processing of these residues in an alkaline medium leads to the production of valuable composite materials with a compressive strength greater than 20 MPa at room temperature and approximately 60 MPa at 1000°C. Through geopolymerization, RM and RH are not stored in piles or dumped into nature ; this is a considerable achievement for the circular economy and the *zero waste* principle.

References

- [1]. Dipak K, Sarkar (2015) : Steam Generators, In Thermal Power Plant, Elsevier, Pages 39-89, ISBN 9780128015759, <http://dx.doi.org/10.1016/B978-0-12-801575-9.00002-0>.
- [2]. Patricia Córdoba (2015) : Status of Flue Gas Desulphurisation (FGD) systems from coal-fired power plants: Overview of the physico-chemical control processes of wet limestone FGDs, Fuel, Volume 144, 15 March, Pages 274-286, ISSN 0016-2361, <http://dx.doi.org/10.1016/j.fuel.2014.12.065>
- [3]. Matthews, F.L.; Rawlings, R.D. (1999) : Overview. In Composite Materials: Engineering and Science, 2nd ed.; CRC Press, Woodhead Publishing Limited: Cambridge, UK, pp. 1–28. [Google Scholar]
- [4]. Tanaka, T.; Montanari, G.C.; Mülhaupt, R. (2004) : Polymer nanocomposites as dielectrics and electrical insulation—Perspectives for processing technologies, material characterization and future applications. IEEE Trans. Dielectr. Electr. Insul. , 11, 763–784. [Google Scholar] [CrossRef]
- [5]. Power G, Gräfe M, Klauber C. (2011) : Bauxite residue issues ; Current management, disposal and storage practices, Hydrometallurgy ;108 :33–45
- [6]. J. Hausberg, U. Happel, F. M. Meyer J. Schlimbach, G. Rombach: Bauxite quality and its effect on red mud generated during alumina production ; International Symposium on Mine Environmental and Economical Issues, Dnipropetrovsk, Ukraine, Russia, June 1999.
- [7]. Renfortha, P. ; Mayesb, W. M.; Jarvisc, A.P.; Burked, I.T. Manning, D. C. (2012) : Science, K. Contaminant mobility and carbon sequestration downstream of the Ajka (Hungary) red mud spill: The effects of gypsum dosing, Sci, Total Environ, 421–422, 253–259.
- [8]. Tamotia SK, Management of red mud, In: International symposium on processing of fines, vol, 2, Jamshedpur: NML Jamshedpur; 2000, p, 430–4.
- [9]. Okutani, T, and Nakata, Y. (1996) : Industrial utilization of silica in rice hulls, J, Jpn,Soc, Calorimetry Thermal Analys, (Netsu Sokutei), 23 : 117-127,
- [10]. J, James, M,S, Rao, (1985) : Thermochim.; Acta 97, 329
- [11]. R,V, Krishnarao, J, Subrahmanyam, T,J, Kumar (2001) : J. Eur, Ceram.Soc, 21 99 .
- [12]. W. Xu, T.Y. Lo, S.A. Memon (2012) : Microstructure and reactivity of rich husk ash, Constr. Build. Mater. 29 ;541–547
- [13]. Davidovits J. (1991) : J. Therm. Anal 37:1633.
- [14]. Hart R. D., Lowe J. L., Southam D. C. , Perera D. S. ; Walls, P. Vance E. R., Gourley T., Wright K. (2006) : Aluminosilicate inorganic polymers from waste materials. In Proceedings of the third international conference on sustainable processing of minerals and metals, green processing ; (vol,2006),
- [15]. Davidovits, J. (2014) : Chimie des Géopolymères, Techniques de l'Ingénieur N3300 V1.
- [16]. Avraamides J, van Riessen A, Jamieson E. (1976) : Transforming mining residues into viable by-products, Energy Gener 2010:1–3, polycondensation of alumino-silicate polymers : Na-poly(sialate) or Na-PS and characteristics. IUPAC Symposium on Long-Term Properties of Polymers and Polymeric Materials, Stockholm
- [17]. Davidovits J. (1976) : Solid-phase synthesis of a mineral blockpolymer by low temperature polycondensation of alumino-silicate polymers : Na-poly(sialate) or Na-PS and characteristics. IUPAC Symposium on Long-Term Properties of Polymers and Polymeric Materials, Stockholm
- [18]. D. R. Kumar, A. Kumar, K. N. Rai (2008), Ceramica, 54, 203.

- [19]. Shinohara Y, Kohyama N. (2004) : Quantitative analysis of tridymite and cristobalite crystallized in rice husk ash by heating. *Ind Health* ; 42(2):277–85.
- [20]. Shinohara Y., Kohyama N. (2004) : Quantitative analysis of tridymite and cristobalite crystallized in rice husk ash by heating. *Ind Health* 42(2):277–85.
- [21]. D. R. Kumar, A. Kumar, K. N. Rai (2004) : *Ceramica* 2008, 54, 203.
- [22]. S. Traoré, S. Diakité, D. L. Traoré (2014) : *Int. J. Mater Eng.*, 4, 25.
- [23]. Z. Pan, G. Jay, G. Kong (2012) : *Constr. Build. Mater.*, 36, 365
- [24]. Standard ASTM C55 99, Standard specification for concrete brick.