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Effect of Temperature in Unglazed Ceramic Tile Production by replacement of Feldspar with Glass Cullet and Spent Silica-Alumina
ผลของอุณหภูมิในการผลิตกระเบื้องเซรามิกแบบไม่เคลือบจากการทดแทนแร่เฟลด์สปาร์ด้วยเศษแก้วสีเขียวและซิลิกา-อะลูมินาที่ใช้แล้ว

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Abstract

The objective of this research is to replace feldspar by using green glass cullet and spent silica-alumina in ceramic tile body. The ratio of ball clay with green glass cullet and spent silica-alumina used in this research was 8:5 which represented 60% of the total amount. The composite was then mixed with 40% of silica sand by using ball mill. The mixture was pressed into tiles with the size of 10 x 10 x 0.5 cm^3 under the pressure of 100 bars and firing at 1150 ^{o}C and 1200^{o}C. The physical property was analyzed according to the standard set by the Thailand Industrial Standard ref. In order to save energy during the production process, the appropriate ratio and temperature were selected. The result indicated that the mixture with the ratio between green glass cullet and spent silica-alumina of 35:65 and burned at 1150^{o}C could pass the Thailand Industrial Standard of floor tiles (TISI 37-2529) and the Thailand Industrial Standard of wall tiles (TISI 614-2529). The mixture had the quantity of bending strength equal to 28.76 MPa, a firing shrinkage equal to 12.41% and the water absorption equal to 3.62%. The result obtained from X-ray diffraction indicated that the mullite phase which increases the strength of the ceramic tile was found.

Keywords : Green Glass Cullet; Spent Silica-Alumina; CeramicTile; Mullite Phase

บทคัดย่อ

งานวิจัยนี้นำเศษแก้วรีไซเคิลสีเขียวและซิลิกา-อะลูมินาที่ใช้แล้วมาทดแทนเฟลด์สปาร์ โดยมีอัตราส่วนผสมวัตถุดิบในการผลิตกระเบื้องเซรามิก คือ ดินดำต่อเศษแก้วสีเขียวและซิลิกา-อะลูมินาที่ใช้แล้ว 8 ต่อ 5 คิดเป็นร้อยละ 60 ของส่วนผสมทั้งหมด รวมกับทรายแก้วอบแห้งร้อยละ 40 ผสมด้วยหม้อบดขึ้นรูปเป็นแผ่นกระเบื้องขนาด 10 x 10 x 0.5 ซม^3 ด้วยความดันการอัดขึ้นรูป 100 บาร์ เผาที่อุณหภูมิ 1150 และ 1200 องศาเซลเซียส นำไปทดสอบลักษณะสมบัติทางกายภาพตามมาตรฐานอุตสาหกรรมโดยอัตราส่วนการทดแทนและอุณหภูมิที่เหมาะสมจากการวิเคราะห์ทางด้านเศรษฐศาสตร์เพื่อช่วยประหยัดพลังงานในกระบวนการผลิตคืออัตราส่วนการทดแทนแร่เฟลด์สปาร์ด้วยเศษแก้วสีเขียวและซิลิกา-อะลูมินาที่ใช้แล้วเป็นร้อยละ 35:65 ผ่านการเผาที่อุณหภูมิ 1150 องศาเซลเซียส ซึ่งมีลักษณะสมบัติในด้านกำลังรับแรงดัด 28.76 เมกกะปาสคาล ค่าการหดตัวร้อยละ 12.41 ค่าการดูดซึมน้ำร้อยละ 3.62 และผลการวิเคราะห์เฟสด้วยวิธีเอ็กซเรย์ดิฟแฟรกชั่น (XRD) พบเฟสมัลไลท์ซึ่งเป็นเฟสที่ทำให้เกิดความแข็งแรงในกระเบื้องเซรามิกได้

คำสำคัญ : เศษแก้วสีเขียว; ซิลิกา-อะลูมินาที่ใช้แล้ว; กระเบื้องเซรามิก; เฟสมัลไลท์

Introduction

Due to the hydrogen peroxide processing, spent silica-alumina is produced at around 100 tons per year mainly composing of alumina (Al_2O_3), silica (SiO_2) and sodium oxide (Na_2O). Furthermore, there are about 40,000 tons of waste glass per year in the non-recyclable process which is mainly composed of silica (SiO_2), sodium oxide (Na_2O), and calcium oxide (CaO). The aforementioned substances were mainly glass composition but they depend on glass processing. Therefore, the problem of recycling of mixed waste glass occurred. Most of Ceramic industries focus on environmental concern. The industries try to support the utilization of inexpensive raw materials as well as the utilization of waste materials. Waste minimization and waste utilization are the alternative solution for the environmental concern. This research focuses on the possibility of using green glass cullet and spent silica-alumina in order to replace feldspar.

Objectives

This research aimed to study the raw material mixing ratio of ceramic tiles by using green glass cullet and spent silica-alumina in order to replace feldspar. The experiments were carried out in order to investigate the optimum chemical component for the process. The chemical and physical properties of ceramic tiles were investigated and compare to the Thailand Industrial Standard of floor tile (TISI 37-2529) and the Thailand Industrial Standard of wall tile (TISI 614-2529).

Experimental

Raw material

Raw materials used in this research were green recycled glass cullet from recycling factory and spent silica-alumina from hydrogen peroxide industry. Ball clay, feldspar and silica sand are obtained from Sibelco Industry Thailand.

Method

1. Prepared fine grinding raw materials using tube mill and sieved with mesh size of 100.

2. Analysis of raw material chemical composition by X-ray fluorescent (XRF-Phillips model PW2400). The Particle size distribution was analyzed by Mastersizer 2000. The leaching of heavy metal from spent silica-alumina was analyzed by waste extraction test (WET) [1].

3. Prepared wet body mixed by ball mill with added ball clay. The ration between green glass and spent silica-alumina was 8:5 which is equal to 60% of the total amount. The composite was mixed with 40% of silica sand and 50% of water by using ball mill. The slurry contents were dried on a plaster mold in an electric oven at 105°C for 24 hours and then grounded to powder and sieved with the mesh size of 80. After that the powder was sprayed with water to achieved a 10 percent humidity during mixing. The mixing batch was aged for 3 days. The sample ratio of green glass and spent silica-alumina is shown in Table 1 in which ball clay and silica sand constant were 36.92 and 40 respectively. In this research we varied the percentage of green glass and spent silica-alumina as a substitute for feldspar 23.08% in the total mixture. For instance, the green glass and spent silica-alumina ratio were 0:0, 15:85, 25:75, and 35:65.

4. Preparation of ceramic tiles and test method. Mixing powder was sieved with the mesh size of 20 then pressed to make a 10 x 10 x 0.5 cm^3. Tiles are created by a pressing machine under the pressure of 100 bars. The pressed tiles are dried in an electric oven at 105°C for 6 hours before firing. The dried tiles are fired in an electric furnace at 1150 and 1200°C for the heating rate of 3°C per minute and soaking time of 15 minutes [2]. Ceramic tiles after firing were tested using quality standard on floor tiles standard (TISI 37-2529) and wall tile standard (TISI 614-2529) [3, 4].

Result and Discussion

Raw materials used in this research were analyzed, the chemical composition by X-ray fluorescent were reported in Table 2. The main compositions of Ball clay were Silica (60.04%) and Alumina (23.32%). Silica sand consists of 98.9 percent silica. Green glass consists of silica (70.97%) which was close to silica in Feldspar (72.16%). The results indicated that Green glass consists of alumina (1.21%) less than alumina in Feldspar (16.81%). For this reason, the spent Silica-Alumina which consist of silica 11.7% and alumina 54.02% will be useful for as an alternative raw materials.

Table 1 The mixtures compositions of raw materials (%wt)

Formula	Ball clay	Silica sand	Replaced feldspar 23.08 (100%)	
			Green glass	Spent Silica-Alumina
1	36.92	40	0	0
2	36.92	40	3.46 (15%)	19.62 (85%)
3	36.92	40	5.77 (25%)	17.31 (75%)
4	36.92	40	8.08 (35%)	15.00 (65%)

Table 2 Chemical composition of raw material (%wt)

Chemical composition	Raw material				
	Ball clay	Silica sand	Green glass	Spent Silica-Alumina	Feldspar
SiO_2	60.04	98.90	70.97	11.7	72.16
Na_2O	0.31	0.02	15.12	3.17	8.00
CaO	0.26	0.03	10.87	0.42	1.07
Al_2O_3	23.32	0.45	1.21	54.02	16.81
MgO	0.67	0.04	0.84	0.00	0.21
Fe_2O_3	1.69	0.04	0.29	0.05	0.22
Cr_2O_3	0.00	0.00	0.24	0.00	0.00
PbO	0.00	0.00	0.02	0.00	0.00
TiO_2	0.63	0.05	0.09	0.00	0.21

The Particle size distribution of raw materials was reported in Table 3. The average particle size of Ball clay, Silica sand, green glass and Feldspar was equal to 0.015, 0.017, 0.127 and 0.026 mm. respectively. The previous research [5-9] reported that the optimum average particle size of Spent Silica-Alumina should be less than 0.147 mm. The Spent Silica-Alumina used in this research was grinded to have an average particle size 0.139 mm. [5]. The leaching of heavy metal from spent silica-alumina was analyzed by waste extraction test as shown in Table 4. The results indicated that the concentration of heavy metals was below the Threshold Limit Concentration (STLC) [1]. The Spent Silica-Alumina used in this research was considered as non-hazardous waste.

Table 3 Average particle size distribution of raw materials

Raw materials	Ball clay	Silica sand	Green glass	Spent Silica-Alumina	Feldspar
Average particle size (mm)	0.015	0.017	0.127	0.139	0.026

Table 4 Leaching of heavy metal from Spent Silica Alumina

Heavy metal	Concentration (mg/l)	Threshold Limit Concentration (STLC) (mg/l)
Zinc (Zn)	1.98	250
Copper (Cu)	0.027	25
Lead (Pb)	<0.09	5.0
Chromium (Cr)	0.064	5.0

The raw materials have a mixture the percentage of ball clay at 36.92 and silica sand at 40 [5]. This research varied the percentage of green glass and spent silica-alumina as 0:0, 15:85, 25:75, and 35:65, which substituted feldspar of 23.08% in the total mixture fired at 1150 and 1200°C. It is found that all ratios of green glass and spent silica-alumina substituting feldspar after firing both temperatures, passed the Thailand Industrial Standard of floor tile (TISI 37-2529) and wall tile (TISI 614-2529). The chemical composition of the body mixed by calculation is shown in Table 5 and similar to the previous research [6, 7]. Physical properties of substituted ratios such as bending strength, water absorption and firing shrinkage after firing at 1150 and 1200°C are shown in Table 6.

Table 5 Chemical composition of the body mixtures (%wt)

Chemical composition	Mixtures composition			
	formula 1	formula 2	formula 3	formula 4
SiO_2	81.36	70.23	71.50	72.78
Na_2O	1.99	1.50	1.75	2.00
CaO	0.37	0.61	0.85	1.08
Al_2O_3	13.75	24.25	22.59	20.93
MgO	0.34	0.32	0.34	0.36
K_2O	1.08	0.88	0.88	0.88
Fe_2O_3	0.77	0.74	0.75	0.75
Cr_2O_3	0.00	0.01	0.01	0.02
PbO	0.00	0.00	0.00	0.00
TiO_2	0.03	0.28	0.29	0.29

Table 6 Physical properties of the fired materials

Physical properties	bending strength (MPa)		water absorption (%)		firing shrinkage (%)	
	Temparature (°C)		Temparature (°C)		Temparature (°C)	
	1150	1200	1150	1200	1150	1200
formula 1 (0 : 0)	25.82	32.19	3.92	1.48	8.39	15.12
formula 2 (15:85)	25.11	30.65	3.94	3.85	8.05	11.51
formula 3 (25:75)	26.61	30.74	3.87	3.06	10.04	14.36
formula 4 (35:65)	28.76	31.04	3.62	2.56	12.41	15.60
TISI 37-2529	not less than 25		not over than 6		unindentified	
TISI 614-2529	not less than 20		not over than 6		unindentified	

By testing the bending strength of ceramic tile after firing at 1150 and 1200°C, it is found that by increasing the percentage of green glass and spent silica-alumina as 15:85 25:75 and 35:65, the bending strength is increased. Firing at 1150°C provided the bending strength of 25.11 26.61 and 28.76 MPa, respectively and the percentage of substituted ratio 35:65 provided the most bending strength when compared with substituted ratio 0:0 providing 25.82 MPa. This temperature was in the range of glass melting and the melted glass acted as fluxing agent which were well-coordinated raw materials [8].

Therefore, the ceramic tile bending strength depends on the amount of glass and spent silica-alumina which were added as substitute in this research in order to perform mullite crystal on ceramic tile. The suitable ratio of alkaline and alkaline earth group as well as silica content has to be adjusted. The role of silica is to control glass phase to high viscosity and effected on crystal formation [9]. At 1200°C it was found that the increased percentage of green glass and spent silica-alumina at 0:0 15:85 25:75 and 35:65 provided the bending strength of 30.65 30.74 and 31.04 MPa, respectively. The percentage of substituted ratio of 35:65 provided the bending strength less than the substituted ratio of 0:0 which provided the bending strength of 32.19 MPa. Because this temperature was in the range of feldspar melting and the melted feldspar acted as fluxing agent which coordinated raw materials better than glass. Therefore, the bending strength of all substituted ratios is less than the substituted ratio of 0:0. By testing the firing shrinkage of ceramic tile after firing at 1150°C, it is found that the increased percentage of green glass and spent silica-alumina at 15:85 25:75 and 35:65 provided increased percentage of firing shrinkage of 8.05, 10.04 and 12.41, respectively. The percentage of substituted ratio of 35:65 provided the most firing shrinkage when compared with substituted ratio of 0:0 which provided 8.39. This result corresponded to bending strength such as when increasing the bending strength, the firing shrinkage increases and the result is similar for 1200°C with increased percentage of firing shrinkage of 11.51, 14.36 and 15.60, respectively. However, the temperature influenced the firing shrinkage and the same mixture at higher firing temperature caused more firing shrinkage.

By testing water absorption of ceramic tile after firing at 1150°C it is found that the increased percentage of green glass and spent silica-alumina were 15:85 25:75 and 35:65, provided decreasing percentage of water absorption of 3.94, 3.87 and 3.62, respectively. And the percentage of substituted ratio 35:65 provided the least water absorption when compared with substituted ratio 0:0 which provided water absorption 3.92. Moreover, 1200°C provided decreasing percentage of water absorption of 3.85, 3.06 and 2.56, respectively. This result corresponded to bending strength and firing shrinkage. Higher bending strength and higher firing shrinkage provided strong ceramic tile but with decreased value of water absorption. From the research of [10] it is found that the substituted percentage of green glass and spent silica-alumina were 15:85 by wet mixing process and firing at 1200°C and soaking time of one hour. It is found that ceramic tiles after firing could pass the Thailand Industrial Standard of floor tile (TISI 37-2529) and wall tile (TISI 614-2529) and provided bending strength of 29.22 MPa, percentage of water absorption 4.16 and firing shrinkage of 27.94. For this research, the substituted percentage ratio were 15:85 by wet mixing ball mill and firing at 1200°C with soaking time 15 minute. It is found that ceramic tiles after firing could pass the Thailand Industrial Standard of floor tile (TISI 37-2529) and wall tile (TISI 614-2529) and provided bending strength of

30.65 MPa, percentage of water absorption 3.85 and firing shrinkage of 11.51. However, the higher bending strength the decreases in water absorption and firing shrinkage. This result follows the theory which informed that "fast firing effect on well glass phase flow in order to support strength of the ceramic tile" [11].

Furthermore, X-ray diffractometry examination shown in Figures 1 and 2 found that the percentage of green glass and spent silica-alumina were 0:0 15:85 25:75 and 35:65, the substituted percentage of feldspar was 100 after firing at 1150°C and 1200°C. For studied on Ceramic Tile after fired mainly phase such as quartz (SiO_2), crystobalite (SiO_2) and especially mullite ($3AlO_3 2SiO_2$) are occurred and effected on product strengthen [12, 13]. The mechanism of Silica phase and alumina phase melting and forming the mullite phase resulted in the strength of the product as described in the previous research [14].

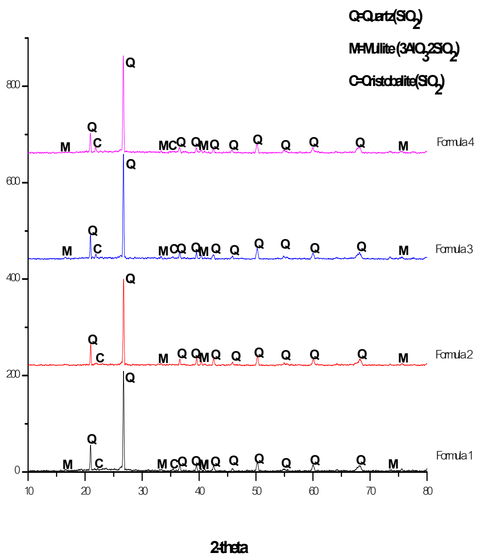

Figure 1 XRD analysis, Ceramic Tile of formula 1 to 4, fired at 1150°C.

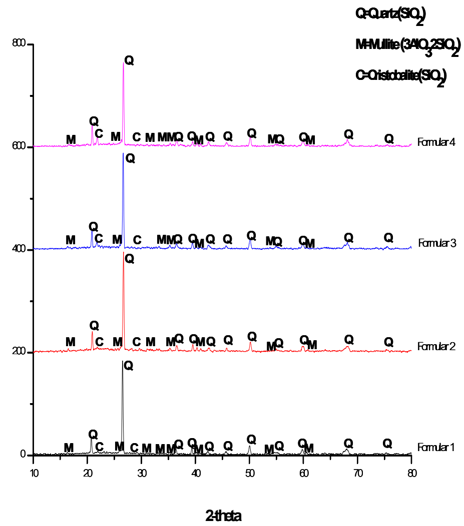

Figure 2 XRD analysis, Ceramic Tile of formula 1 to 4, fired at 1200°C

Conclusion

From the study of green glass and spent silica-alumina with adjusted ratios for substitution of feldspar, it is found that they could be used as raw materials to substitute feldspar as fluxing agent in ceramic tile production. The optimal substituted feldspar by using percentage of green glass and spent silica-alumina was 35:65 after firing at 1150°C. And it is found that the main important chemical compositions of the body mixture are SiO_2 72.78%, Al_2O_3 20.93%, CaO 1.08% and Na_2O 2.00% respectively. Ceramic tiles after firing had a bending strength of 28.76 Mpa, the percentage of water absorption 3.62 and firing shrinkage 12.41 and could pass the Thailand Industrial Standard of floor tile (TISI 37-2529) and wall tile (TISI 614-2529). Moreover, mullite phase occurred and affected the strength of ceramic tile. Hence firing at 1150°C was appropriate economically for energy saving in the production process.

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