Characterization and performance analysis of a new stoneware

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Abstract. Guangdong Baojue New material Industry Co., Ltd fired stoneware with local rock and ore as main raw material. The material and properties of stoneware were characterized in this paper. The composition of stoneware was analyzed by inductively coupled plasma emission spectroscopy (ICP-AES) and X-ray fluorescence spectroscopy (XRF). The phase composition and microstructure of stoneware were analyzed by XRD and metallographic microscope. In this paper, the full-emittance, the air negative ion concentration, the content of the toxic component and the chlorine-removing ability were tested, and the soaking test of the Chinese liquor was carried out. The results showed that stoneware was an excellent material for drinking utensils and was beneficial to human health.

1. Introduction
Stoneware is a stoneware ware that is somewhere between stoneware and porcelain. It is similar to stoneware but different from stoneware [1]. Stoneware is made of vitrification (similar to glass, liquid impermeable) at about 1200 °C. Its quality is dense, natural mud color is taken, no water absorption, and the sound is coarse and long [2]. In recent years, stoneware industry has developed rapidly, because it belongs to green environmental protection ceramics, it is favored by domestic and foreign users, and the products are sold well all over the world. Our country is a big country producing stoneware. At present, the demand of domestic users for stoneware is increasing, and the quality requirement is becoming higher and higher [3]. Guangdong Baojue New material Industry Co., Ltd uses local rock and ore as the main raw material. Through scientific research and optimization into mud, new stoneware products with unique style have been developed and put on the market. It has contributed to the development of stoneware industry in China. This paper takes stoneware as the research object, studies its material composition and analyzes its performance.

2. Composition and phase analysis

2.1. Composition analysis
The stoneware powder was analyzed by inductively coupled plasma emission spectra. As many as 15 kinds of elements were detected, among which Si, Fe and Ca were in high content, and trace elements included P, Zn and Se, as shown in table 1.
Figure 1. Photos of stoneware raw ore powder.

Table 1. Element composition of stoneware raw ore powder.

| Element | Content (mg/kg) | Element | Content (mg/kg) |
|---------|----------------|---------|----------------|
| V       | 6.6            | Zn      | 37             |
| Cr      | 12.4           | K       | 1.70×10³       |
| Si      | 2.32×10³       | Ca      | 6.38×10³       |
| Mn      | 146            | Na      | 158            |
| Mo      | <2             | Mg      | 4.14×10³       |
| Sr      | 11             | P       | 294            |
| Cu      | 10             | Fe      | 1.64×10⁴       |
| Se      | <5             |         |                |

The chemical composition of stoneware raw ore powder was tested by X-ray fluorescence spectrometer, as shown in Table 2. It can be seen that stoneware raw ore mainly includes SiO₂, Al₂O₃, Fe₂O₃, as well as P, Zn and other trace element oxides.

Table 2. Chemical composition of stoneware minerals.

| Element   | Content (wt%) | Element   | Content (wt%) |
|-----------|---------------|-----------|---------------|
| SiO₂      | 65.46         | BaO       | 0.136         |
| Al₂O₃     | 19.24         | CaO       | 0.130         |
| K₂O       | 5.73          | Na₂O      | 0.108         |
| Fe₂O₃     | 5.49          | ZrO₂      | 0.0365        |
| MgO       | 2.58          | Rb₂O      | 0.0324        |
| TiO₂      | 0.840         | Cr₂O₃     | 0.0133        |
| P₂O₅      | 0.190         | ZnO       | 0.0100        |

2.2. Phase analysis

The phase composition of stoneware raw powder was analyzed by X-ray diffractometer (XRD), and the stoneware sample after firing was analyzed. It can be seen from the diffraction diagram that the phase composition of the raw ore powder is mainly quartz, Muscovite and hematite. The stoneware phases after firing are mainly quartz, mullite and hematite. The phase of trace elements can not be detected by X-ray diffraction.

Figure 2. XRD analysis: (a) Stoneware ore powder; (b) Stoneware.
2.3. Metallographic analysis
The microstructure of ceramics was observed by confocal laser microscopy. It can be seen that stoneware has fine tissue, a large number of granular quartz in the matrix, and red iron minerals with small particles. The dark mass phase in stoneware is mullite.

![Figure 3. (a) Stoneware appearance photos; (b) Photos of stoneware tissue analysis](image)

3. Performance analysis

3.1. Toxic component test
The toxic components of stoneware cadmium, lead, mercury, hexavalent chromium and polybrominated biphenyl (PBBs), polybrominated diphenyl ether (PBDEs) were tested by Standard Technical Services Co., Ltd. The test results do not exceed the limit requirements of the revised (EU) 2005/863 of the EU RoHS Directive 2011/65/EU Appendix II, as shown in Table 3.

| Test project                                      | limit | unit  | MDL | 001 |
|--------------------------------------------------|-------|-------|-----|-----|
| Cd                                               | 100   | mg/kg | 2   | ND  |
| Pb                                               | 1000  | mg/kg | 2   | 20  |
| Hg +6Cr                                          | 1000  | mg/kg | 2   | ND  |
| Sum of polybrominated biphenyls (PBBs)           | 1000  | mg/kg | -   | ND  |
| Bromobiphenyl                                    |       | mg/kg | 5   | ND  |
| Dibromobiphenyl                                  |       | mg/kg | 5   | ND  |
| Tribromobiphenyl                                 |       | mg/kg | 5   | ND  |
| Tetrabromobiphenyl                               |       | mg/kg | 5   | ND  |
| Pentabromobiphenyl                               |       | mg/kg | 5   | ND  |
| Hexabromobiphenyl                                |       | mg/kg | 5   | ND  |
| Heptabromobiphenyl                               |       | mg/kg | 5   | ND  |
| Octabromobiphenyl                                |       | mg/kg | 5   | ND  |
| Nonabromobiphenyl                                |       | mg/kg | 5   | ND  |
| Decabromodiphenyl                                |       | mg/kg |     | ND  |
| Sum of polybrominated biphenyls (PBDEs)          | 1000  | mg/kg | -   | ND  |
| Monobromobiphenyl                                |       | mg/kg | 5   | ND  |
| Dibromodiphenyl                                  |       | mg/kg | 5   | ND  |

The content of soluble lead and cadmium in stoneware was tested. The test results meet the requirements of EU food grade testing certification and North American food grade testing certification, as shown in Table 4.
Table 4. Chemical composition of stoneware minerals.

| Soluble element | EU food grade testing certification (μg/mL) | North American food grade testing certification (μg/dm²) |
|-----------------|--------------------------------------------|---------------------------------------------------|
|                 | test value | limited value | test value | limited value |
| Pb              | <0.05      | 0.5           | <0.1       | 0.8          |
| Cd              | <0.01      | 0.5           | —          | —            |

3.2. Normal total emissivity

The normal emissivity of stoneware is 0.87 at 80 °C. Far infrared rays can be released during heating of stoneware. The frequency of far infrared ray is the same as the rhythm of water molecules in biological cells, which is easily absorbed by the human body. Therefore, it radiates heat energy from the inside out, activates tissue cells, keeps warm, promotes metabolism, and increases the body immunity. It has a significant effect on the prevention and treatment of arthritis, cardiovascular disease, diabetes and other diseases [4].

3.3. Air anion concentration

The negative ion concentration of stoneware reached 2580/cm³ after being tested by the National testing Center for Building Materials. Negative ions can promote the synthesis and storage of vitamins, enhance and activate the physiological activities of the human body, so it is also known as "air vitamins." Liquid anion water has smaller molecular clusters, shorter molecular chains, easier infiltration of cell membranes, easier transport of reactive oxygen species and nutrients, and provision of nutrients and energy to cells.

3.4. Dechlorination ability test

The removal ability of free residual chlorine in water of stoneware was tested. Stoneware cup and laboratory clean glass beaker were compared under the same conditions. When the free residual chlorine concentration is 0.1 microns/mL, the stoneware cup and the glass beaker have been kept under the same conditions for 4 hours, the amount of free residual chlorine in the water is 40% smaller. The experiment shows that the use of this kind of stoneware cup to make tea can improve the taste of tea, and can improve the taste of tea.

3.5. Liquor soaking test

The change of liquor composition in stoneware cup was tested by HS-GC-MS, and the filling time was 10 min. The purpose of this study was to analyze the effect of stoneware cup on liquor taste. The most kinds of aroma substances in liquor are esters, and the most important ones are ethyl acetate, ethyl butyrate, ethyl caproate and so on. Increase of ethyl acetate content in white wine after stoneware porcelain cup is filled with 10min. Ethyl acetate, like apple, banana aroma, can effectively improve the taste of liquor. N-butanol has solvent smell, irritation, slightly wet bitter, its content with the prolongation of liquor storage time showed an overall upward trend, the corresponding flavor characteristics will be more and more obvious [5]. The content of n-butanol in stoneware porcelain cup filled liquor 10min showed an increasing trend, which was consistent with the change trend of natural placing of liquor. Glycerol formaldehyde is usually used as the solvent of pesticide and drug injection, and it is the unfavorable component that affects the taste of liquor. The content of glycerol formaldehyde decreased after 10min of stoneware cup filled liquor. There was no obvious change in other components of liquor during the experiment.
Table 5. Composition of white wine before and after stoneware cup dressing.

| Matching substance | Relative percentage /% | Before dressing up for 10min | Matching substance | Relative percentage /% |
|--------------------|-------------------------|----------------------------|--------------------|-------------------------|
| ethanol            | 89.08                   | ethanol                    | 86.63              |
| N-butyl alcohol    | 0.21                    | N-butyl alcohol            | 0.26               |
| Ethyl acetate      | 8.74                    | Ethyl acetate              | 11.14              |
| Sec-butyl alcohol  | 0.04                    | Sec-butyl alcohol          | 0.04               |
| Isobutyl alcohol   | 0.23                    | Isobutyl alcohol           | 0.24               |
| Isovaleraldehyde   | 0.03                    | Isovaleraldehyde           | 0.03               |
| Propionic acid ethyl ester | 0.01          | Propionic acid ethyl ester | 0.02               |
| glycol             | 0.85                    | glycol                     | 0.89               |
| Isoamyl alcohol    | 0.31                    | Isoamyl alcohol            | 0.31               |
| 2-methyl butanol   | 0.06                    | 2-methyl butanol           | 0.05               |
| Ethyl butyrate     | 0.03                    | Ethyl butyrate             | 0.05               |
| Glyceropetal       | 0.37                    | Glyceropetal               | 0.29               |
| Isoamyl acetate    | 0.01                    | Isoamyl acetate            | 0.02               |
| Pentanoic acid ethyl ester | 0.01    | Pentanoic acid ethyl ester | 0.01               |
| Ethyl n-caproat    | 0.02                    | Ethyl n-caproat            | 0.02               |

4. Conclusion
Stoneware is an important inorganic non-metallic material for daily use. In this paper, the composition and properties of stoneware made in Guangdong Baojue New material Industry Co., Ltd are studied. The stoneware consists mainly of quartz, mullite, hematite and some trace elements. At 80 °C, the normal emissivity of stoneware was 0.87 and the concentration of negative ions in stoneware was 2580/cm³. It has excellent removal ability of free residual chlorine in water, which can improve the taste of liquor.

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