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Characteristics of silicate glasses derived from vitrification of manganese crust tailings

G.F. Terry Lay [a,*], Maria C. Rockwell [a], John C. Wiltshire [b], Chefi Ketata [a]

[a] Department of Civil and Resource Engineering, Dalhousie University, 1360 Barrington St., Halifax, Nova Scotia, B3J 1Z1, Canada
[b] Hawaii Undersea Research Institute (HURL), MSB 303, 1000 Pope Rd, Holmes Hall 402, 2540 Dole St., Honolulu, HI 96822, USA

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Abstract

Potential marine manganese crust mining operations will produce millions of tons of tailings requiring waste volume reduction and segregation from their surroundings. To address this situation, the tailings have been vitrified at 1160 °C for 30 min employing various additions of silica sand with borax flux. Resulting silicate glasses displayed microhardness (H_v) of 5.36 GPa, indentation fracture toughness (K_c) of 0.71 GPa, elastic modulus (E) of 98, thermal expansion coefficient (TEC) of 2.75×10^{-6} and excellent resistance to leaching. Study results indicate that vitrification technology is effective for stabilizing, volume reduction and recycling of tailings wastes, while also producing potentially marketable commercial glasses.

Keywords: A. Firing; B. X-ray methods; C. Mechanical properties; D. Glass; E. Structural applications

Marine crust deposits have been extensively studied as potential mineral sources, especially for the very valuable minerals cobalt and palladium [1]. Tailings waste resulting from processing of manganese crust ore in a commercial or dressing plant will require treatment to decrease volume and potential toxicity. The nearest potential land-based processing plants for manganese crust deposits mined in the South Pacific would be on small, environmentally sensitive islands. It is extremely unlikely that the main existing method of tailings treatment (i.e. tailings impoundment) would be an acceptable approach on these islands, where geographic space is very limited, aesthetics are crucial to commerce and the indigenous people hold nature in high regard. Impoundment also does nothing to diminish tailings volume. Recycling and reuse would be the optimal approach based largely upon economic feasibility. Even if tailings impoundment was acceptable under intense scrutiny, this method poses serious risks from possible groundwater pollution due to leachates [2], and potential for catastrophic dam failure [3,4].

Vitrification has been proven to be an effective method of converting waste materials into useful products [5] and treating; hazardous radioactive wastes [6–9], industrial wastes such as fly ash [10,11] and other industrial wastes [12–16]. In addition, vitrification has been shown to be a useful method for treating hazardous mineral ore tailings [17–21] and thus, a possible alternative approach to tailings impoundment, which would be especially applicable to regions where land surface area is at a premium and the environmental and natural aesthetics are considered very important to the local population.

Commercial glass is primarily made of (a) a glass former like silica, (b) alkalis like soda and potash to change the state from solid to liquid, (c) stabilizers like CaO, MgO and Al_2O_3 to reduce weathering, (d) refining agents like Na_2O, K_2O and $CaSO_4$ to remove bubbles, and small quantities of other additives to give different characteristics to the glass [22]. Development of a glass formulation for waste materials represents a challenge with respect to optimising: (a) waste acceptability, (b) melt processability, (c) glass product durability, and (d) overall economics. The acceptability criterion [10] is essential for the product to function as a barrier against the release of heavy metals or other hazardous wastes into the environment.

* Corresponding author. Tel.: +1 902 494 3975.
E-mail address: tlay@dal.ca (G.F. Terry Lay).

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McMillan [23] suggested that silica is not always the major former, since boric oxide has partially or completely replaced silica oxide to produce glasses that exhibit flow characteristics, which make them suitable for special applications. Pelino et al. [24] reported the higher the silica content in the raw materials, the higher the melting temperature. Barbieri et al. [25] suggested that suitable glasses can only be obtained if a satisfactory ratio between glassy network formers and modifiers exists. In addition, the authors described how transition oxides acted as nucleants in a calcium aluminosilicate glass. Common fluxes (e.g. Na_2O, K_2O, LiO_2 and B_2O_3) can reduce the melting temperature of silicate melts, where the melting point of silica is usually (>2000 °C), although adding large amounts of alkali fluxes can degrade chemical durability. Fortunately, this may be offset by adding modifiers such as Al_2O_3 or transition element oxides such as Fe_2O_3 or MnO_2 [26].

The viscosity of a glass melt, as a function of temperature, is the most important variable affecting the melting rate and pourability of the glass. The viscosity determines the rate of melting of the raw feed, the rate of gas bubble release (foaming and fining), the rate of homogenization, and thus the quality of the final glass product. Barbieri et al. [25] reported that melts containing higher alumina content (>15 wt%) have displayed higher viscosity values. Volatility of the melt (foaming) relates to the rate and amount of bubble release, the degree of homogenization and thus the quality of the final glass product.

The slowest cooling rate that produces a glass is deemed the critical cooling rate. Glass stability is often characterized by the difference between the onset of the glass transition region (T_g) and the first occurrence of a crystallization peak (T_p). Lack of distinct exothermic peaks may be taken as lack of crystallization [26]. Acosta et al. [27] reported that power plant derived glass was considered stable due to lack of clear exothermic peaks in the DTA curve. Shelby [26] reported that, slow cooling of glass melts tends to diminish the occurrence of thermal shock and weakening of the glass.

The Vickers microhardness of known oxide glasses ranges from 2 to 8 GPa, while a theoretical strength (K_c) of 32 GPa is typical for silicate glasses. Due to flaws in glass surfaces, actual strengths are much lower. Alumina ions replacing modifier ions in silicate glass reduce the number of non-bridging oxygen ions, which increases the connectivity of the network and subsequently increases the elastic modulus. Since (E) is related to bond strength, it follows that glasses with high glass transformation temperatures usually have high (E) values. The optimal thermal shock resistance is found in low expansion (low α) and low modulus (low E) glasses [26].

Commercial glasses must be resistant to the environment in which they are used. The main factors controlling the rate and mechanism of attack on silicate glasses by aqueous solutions are glass composition, pH of the solution, and the temperature [28]. Chemical resistance of waste glasses is directly related to the extent these glasses resist chemical reactions with water and associated chemicals. Waste glasses undergo a variety of complex changes in aqueous environments, which is referred to as glass corrosion or glass dissolution [29,30]. As industrial materials, glasses should have acceptable durability, which is often linked to high mechanical strength [31]. Sheng et al. [11] reported that using minimum additives, lowering process temperature, decreasing waste volume and producing marketable products are major factors affecting overall economics of turning waste into glass.

Past researchers have demonstrated that it was possible to vitrify various ore tailings with or without additives. These past works have not dealt with the management of manganese crust derived tailings and whether they can be vitrified into a glassy material, which may be reusable. This paper reports on the vitrification behavior of manganese crust tailings, general characteristics of the resulting glassy materials and the potential to use these products as construction materials to offset the cost of tailings treatment.

1. Materials and methods

Manganese crust tailings (slimes) were received from the BHP Billiton mineral processing plant at Groote Eylandt in Northern Australia. The mineral ore was mined from an exposed, previously submerged seamount off the coastline and is considered quite similar to existing deep-sea crust deposits. The slimes arrived as a fine powder, light grey in colour. A Hitachi S-4700 SEM was employed to determine the average size range of tailings grains. It was attempted to form glass with slimes alone, but it was found that an additional former or flux was required. Addition of various weight percentages of inexpensive additives such as silica (silica sand) with slimes, then sodium (sodium bicarbonate) with slimes was attempted, but acceptable glasses could not be produced. Lastly, various percentages of slimes plus a borax flux (sodium tetraborate decahydrate) and silica sand were mixed in weight percentages ranging from 50 to 70 wt% tailings and 30 to 50 wt% borax and substituting 5–20 wt% silica for the other two components, to produce samples. Raw tailings were mixed for 15 min with the borax and silica additives in a ball mill (without the balls), then melted and held for approximately 30 min in clay crucibles in a lab furnace. The melts were then permitted to slowly (5–10 °C per minute) cool to 480 °C, where they were annealed for 1 h, then slowly air cooled to room temperature in the furnace. Shelby [26] noted that a temperature of 50 K above the T_g from DTA curves is usually an adequate annealing temperature. Five promising glasses were identified, while for this study, glass 4-21 (70/30 tailings to flux) was chosen as optimal for extensive testing purposes. The chemical composition of the as-received raw slimes and commercial flux were determined using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The melting range of the raw tailings was determined in a laboratory furnace.

Several techniques were employed to assess mechanical, physical and chemical properties of samples of glass 4-21. A Phillips PW 1720 XRD unit was employed to determine the mineralogical character of the raw tailings and to detect possible crystallization in the heated mixture of slimes and flux. The glass transition temperature (T_g), possible exothermic crystallization peaks (T_p) and the melting point were determined using the DTA/TGA SDT Q600 series unit from TA Instruments. The DTA

thermal analyses were performed at a heating rate of 10 °C/min in an alumina cell with air as the atmosphere and alumina powder (99.9999%) as the reference material. The thermal expansion coefficient (TEC) was determined using the factor of Appen, as follows:

$$\alpha_i = \sum_i \alpha_i p_i \quad (1)$$

where α_i is the partial linear expansion factor for the ith component, and p_i is the mole fraction of the ith glass component. α_i is not considered constant for components that constitute a large fraction of the glass composition, such as SiO_2, B_2O_3, Al_2O_3, MnO_2 and Fe_2O_3 in the study glass compositions. Tables for the partial linear expansion factors according to Appen are found in the work by McLaughlin and Moore [32].

Indentation tests were performed on glass surfaces polished with diamond grit and employing a 1 kg peak load (P) or 5 kg peak load (P). The Vickers hardness value (H_v) was determined in GPa according to the approach by Rincon and Capel [33].

The indentation from the Vickers indenter permits a quick and reliable method of determining fracture toughness (K_c) as the diamond edges create cracks that are easily visible on polished surfaces. Fracture toughness is determined in MPa $m^{1/2}$ using the equation by Evans and Charles [34], where the peak load value was determined as 1 kg load = 49 N. The elastic modulus (E), a measure of strength, was determined theoretically in (GPa) by substituting values determined for H_v and K_c into four known equations and comparing the results for accuracy. The equations are as follows [35–38]:

$$K_c = 0.0363\left(\frac{E}{H_v}\right)^{2/5}\left(\frac{P}{a^{1.5}}\right)\left(\frac{a}{c}\right)^{1.56}, \quad (4)$$

$$K_c = 0.0264(E^{0.5})(P^{0.5})(c^{-1.5})a, \quad (5)$$

$$K_c = 0.036(E^{0.4})(P^{0.6})(c^{-1.5})(a^{0.8}), \quad (6)$$

$$K_c = 0.016\left(\frac{E}{H_v}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right), \quad (7)$$

Density of glasses was measured by the Archimedes method [39], using water as the buoyancy medium. Chemical resistances of 2 g of 4-21 samples ranging in particle size from 0.3 to 0.5 mm were determined as the average amount of weight reduction from 5 trials after holding samples at 95 °C for 1 h in 60 cm^3 in respective solutions of 0.01 mol/l NaOH and 0.01 m/l HCl. The samples were weighed before immersion and heating, then washed and dried weighed after immersion [40].

2. Results and discussion

The AAA results in Table 1 and mineralogical testing confirmed the raw tailings to be comprised mainly of the hydrated clays (pyrolusite, 36%; kaolinite and other silicates, 51%: and silica, plus others), with the main elemental oxides being (SiO_2, Al_2O_3, MnO_2 and Fe_2O_3). The chemical composition of the borax flux (sodium tetraborate decahydrate, <400 μm particle size) is also given in Table 1.

Table 1
Chemical compositions of manganese crust tailings and borax flux in weight percentage.

Oxide	Slimes	Borax	Oxide	Slimes	Borax
SiO_2	28.1		K_2O	0.34	
Al_2O_3	20.3		CaO	0.04	
MnO_2	36.0		MgO	0.14	
Fe_2O_3	5.6	0.002	TiO_2	0.48	
B_2O_3		36.47	H_2O	8.36	46.57
Na_2O		16.47	Others	0.04	0.49
BaO	0.6				

An XRD image of the raw tailings (Fig. 1) is in agreement with the AAA findings and confirms that the main oxides are silica oxide as silica (Q), manganese oxide as pyrolusite (Py), and alumina as kaolinite (Ka). These analyses suggest there are relatively high weight percentages of silica and alumina oxides present, but possibly insufficient formers to produce glasses. Considering, that melting of the tailings without additives produced a slag, additional glass forming ability was deemed required. It was found through experimentation that due to lack of sufficient glass formers, glass could not be formed from tailings alone, nor from tailings with the NaO_2 based additive (sodium carbonate from baking soda), in an economic amount of <50% flux.

Contrary to these findings, it was determined that glasses could be formed with sufficient borax (high in NaO_2 content). In addition, the introduction of boric oxide as a former and fluxing agent produced acceptable quality glasses at approximately 100 °C lower than the raw tailings melting temperature. It is probable that beyond boric oxide acting as a former and flux, that Al_2O_3 might act as an additional former, when in small amounts, while MnO_2, Na_2O (from the borax), Fe_2O_3, K_2O, CaO, MgO and BaO may all have acted as minor fluxes and modifiers to increase the likelihood of glass production.

Glasses formed were dark brown to black in bulk form and dark-brown in powdered form. As the weight percentage of silica in the glass sample mixtures decreased, influence of the iron, manganese and alumina oxides created glasses darker

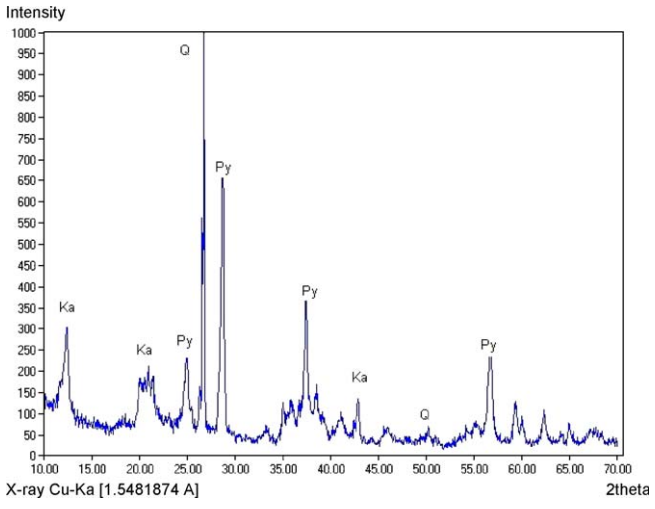

Fig. 1. XRD of as-received raw tailings.

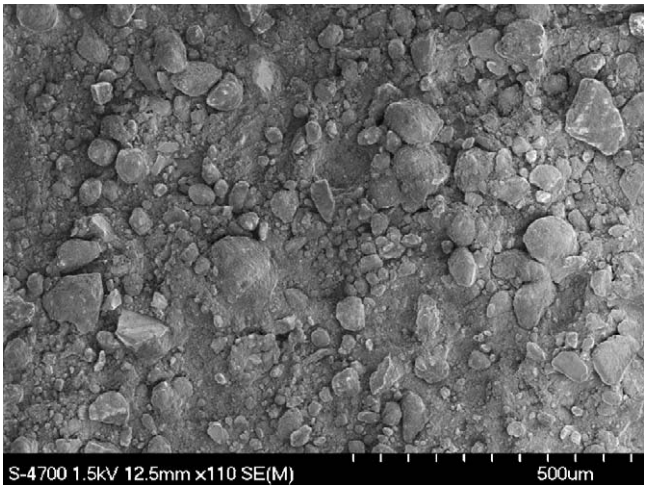

Fig. 2. SEM of as-received manganese crust tailings.

brown in colour. According to an SEM micrograph (Fig. 2), the crust tailings were rounded to angular with a particle size ranging from 10 to 200 μm. The size range of tailings was similar to that of borax powder and within a range that would produce acceptable glasses without the need to employ further crushing or grinding, thus avoiding additional preparation costs. The most promising glasses produced were comprised of mixtures of slimes/borax/silica as 4-20 (65/30/5), 4-21 (70/30/0), 4-22 (50/40/10), 4-23 (55/40/5), 4-24 (60/40/0) and 4-25 (50/50/0). Sample 4-21 was chosen as the optimal sample for extensive testing based upon (colour, clarity, lack of spotting and fractures and apparent homogeneity). Sample 4-25 was of higher quality in many aspects than 4-21, but the latter contained 20 wt% higher tailings content, thus glass 4-21 was chosen for its greater economic significance, that of disposing the maximum volume of tailings, while still producing a potentially useful by-product.

The initial 4-21 glass mixture contains insufficient silica to act as a former, thus the addition of boron oxide in the flux, along with the sodium oxide in the flux and tailings combine with the alumina and magnesium oxide stabilizers from the tailings to promote glass production. The boron and alumina oxides from the flux and tailings, respectively, combine to lower the melt temperature. The small amounts of potassium, calcium and barium from the tailings combine to act as refining agents, while the transition oxides manganese and iron from the tailings act to create specific properties such as high durability. The relatively high alumina oxide content can also be expected to increase the viscosity of the melt, which was observed through the ease of pouring the glass melt.

According to Sheng et al. [11], higher ($SiO_2 + Al_2O_3$) content in the melt leads to higher viscosity values, with the viscosity mainly dependent upon the content of network formers and exhibiting rapid reduction as the percentage of Na_2O is increased. Thus, from the viewpoint of pourability, a 10 wt% Na_2O content was reported as appropriate. Considering that the weight percentage of Na_2O in sample 4-21 of 8-10 wt% is close to the suggested value, the pourability was expected to be acceptable for the 4-21 melt and proved to be so. Viscosity measurement of the glass melts was determined to be infeasible due to the melt frothing in the Brookfield viscosity measuring device.

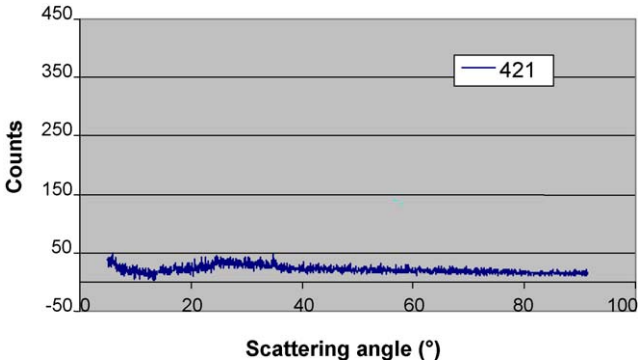

Fig. 3. XRD image of study glass 4-21.

Fig. 3 displays an XRD image of the resultant silica glass 4-21 derived from manganese crust tailings (slimes) and borax indicating the totally amorphous nature of the sample. Fig. 4 is an optical micrograph (20 times) of glass 4-21 showing the glass is apparently phase separated (glass-in-glass) with

Fig. 4. Optical micrograph of study glass 4-21.

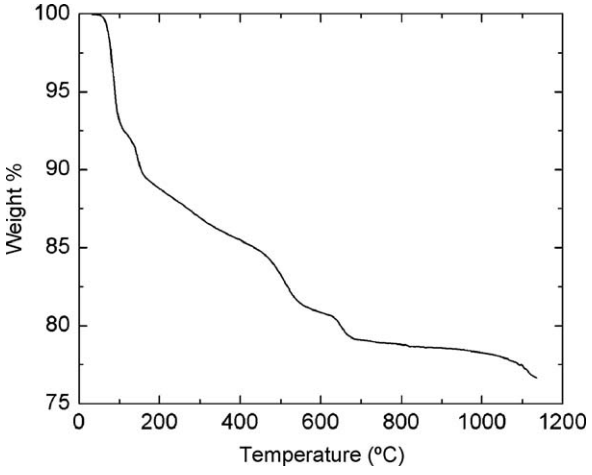

Fig. 5. TGA graph of silicate glass 4-21.

Table 2
Physical characteristics of study glass 4-21 compared to known glasses.

Sample	Density (g/cm^3)	H_v (GPa)	K_{ic} (MPa m^{-6})	E (GPa)	TEC ($\times 10^{-6}$ C^{-1})
4-21	2.50	5.4	0.71	98	2.75
E glass [46]		5.3	0.9	70	
S glass [46]		5.7	1.27	87	
Romero et al. [47]	2.96	5.5	1.1	122	
Appendino et al. [48]	2.60	6.0	0.5	96	100–150
Park and Heo [49]	2.76	5.2	0.92		9.5
Wu et al. [50]	2.90	6.5	0.9	103	9.1

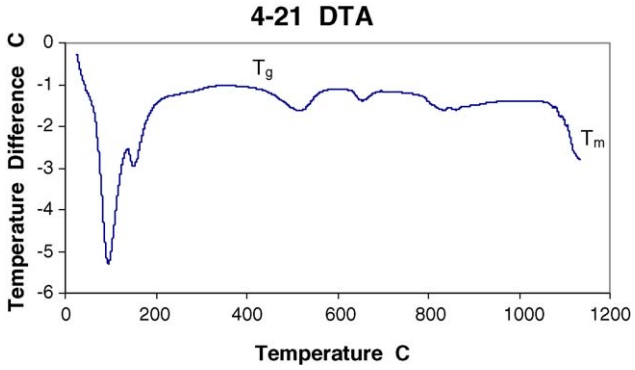

Fig. 6. DTA graph of glass 4-21.

a apparent light coloured matrix phase and possible dark dispersed mineralization as a secondary solute phase. The striations are due to polishing. Quenching of the melt rather than slow cooling, would introduce another processing step and possible increased costs, but could lower the likelihood of phase separation, which can lower the durability of the glass.

TGA observations (Fig. 5) indicated that weight loss from the melt upon heating was over 23% of the initial volume, probably due to loss of oxygen from MnO_2 and Fe_2O_3, hydroxylation of Al_2O_3 rich clays, and water release from the study tailings and borax flux. Unfortunately, there is insufficient database information available to develop a Ternary Diagram for glasses produced from manganese crust tailings and borax flux.

Fig. 6 displays a DTA graph for the 4-21 glass crystals (<200 μm) in which the T_g is represented by the onset of the first endothermic peak at approximately 430 °C. The melting point of the solid phase is located at the endothermic peak at approximately 1160 °C on the DTA curve.

According to evidence by Shelby [26], a major distance between possible indication of crystallization or the lack of definite crystallization peaks may be interpreted as 4-21 being a relatively stable glass. The T_g value of sample 4-21 is relatively low (compared to similar materials produced by Khater [41] and the TEC value (2.75×10^{-6}), from eq. (1), is also rather low, thus according to Shelby [26], the optimal shock resistance should also be relatively low for glass 4-21.

Table 2 gives a comparison of the physical characteristics of study glass 4-21 compared to proven research-based and known industrial glasses, where the study glass compares very favourably, indicating it should be useful for many of the same applications as the known glasses. Sheng et al. [11] reported that up to 15 wt% Na_2O content slowly decreased glass chemical durability in study glasses, while Morita and Suganuma [42] reported that minor weight loss occurred in glasses containing an increasing amount of MnO at the expense of CaO, as long as CaO was still present in the final glass. In addition, Paul and Youssefi [43] reported that MnO substitution for CaO in Na_2O–CaO–SiO_2 glasses improved the alkaline durability at a pH of 10–12. Thus the approximately 9 wt% Na_2O content of the 4-21 glass, due to Na_2O from borax flux, is not considered sufficient to noticeably affect the level of chemical durability. Similarly, the potential weight loss from having approximately 25 wt% MnO in the 4-21 glass mixture along with a nominal CaO content are considered to be offset by the possible improvement in alkaline durability due to the presence of MnO. Chemical resistance determined as the percentage weight loss of sample during heating [40,44] revealed values for the 4-21 glass of 1.42 from a 0.01 mol/l HCl solution and 1.65 from a 0.01 mol/l NaOH solution. The observed values were in the same range as those values exhibited by glass tiles tested under similar conditions [45]. Thus, these results suggest the chemical resistance of glass 4-21 is acceptable compared to known industry glasses.

3. Conclusions and recommendations

The appropriate mixtures of manganese crust tailings, flux and additive can be vitrified to form acceptable quality silicate glasses. Glass forming ability increased in glasses with increasing borax content, suggesting that the borax flux was acting as a flux and network former. As the amount of flux employed increased, the hardness and fracture toughness increased moderately, since borax is acting as a network former and network formers enhance the network connectivity of the glass matrix. The physical and chemical characteristics these glasses compare well with known glasses, which indicates the study glass should be useful in similar commercial applications.

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