MULLITE SYNTHESIS AND FORMATION FROM KYANITE CONCENTRATES IN DIFFERENT CONDITIONS OF HEAT TREATMENT AND PARTICLE SIZE

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Abstract: The process of mullitization of kyanite concentrate was studied at different conditions of heat treatment (1400 – 1600 °C and 0.5 – 3.5 hours) and particle size of raw materials (38-300 ?m). Kyanite concentrate was obtained from ore-dressing of kyanite deposits of Mishidowan-Bafgh region at 100 km northeastern part of Yazd. The results of microstructure (shape, distribution and size of the grains) and phase evolution studies by SEM and XRD showed that total transformation of kyanite to mullite takes place by heat treatment between 1500 –1550 °C during 2.5 hours.. At temperatures below 1500 °C need-like mullite grains are always produced. At higher temperatures the mullite grains reveal rounded and platelet morphology. At 1550 °C, the rate of mullitization and densification were improved by increasing soaking time from 1h to 3h and decreasing particle size of materials from 300 to 38 μm

Keywords: *Kyanite, Kinetic of mullitization, Heat treatments, Densification, Microstructure, Mishidowan-Bafgh deposits*

1. INTRODUCTION

Mullite ($3Al_2O_3.2SiO_2$) as a refractory or ceramic exhibits attractive properties such as high refractoriness, low thermal conductivity, low thermal expansion, good chemical stability and interesting mechanical properties at high temperature. Therefore, mullite is as material which widely used in the manufacture of industrial ceramic [1-4]. High mullite refractories may be commonly achieved by firing natural kyanite group minerals as raw materials comprise anhydrous aluminum silicate polymorphs of andalusite, kyanite and silimanite with the same composition (Al_2SiO_5 or Al_2OSiO_4) [5-15]. Such minerals don't appear on the familiar binary silica-alumina equilibrium phase diagram at one atmosphere pressure [13]. It is due to the three polymorphs compounds are high pressure forms of the 1:1 aluminusilicate that were originally formed at elevated temperature and high pressure in the earth. They are not stable when heated at one atmosphere and are converted into 3:2 mullite and silica at temperature 1300-1600 °C. It depends on the polymorphic form, particles size distribution and impurities level [6,13, 15]:

$$\text{Kyanite} \rightarrow \text{Mullite} + \text{Crystoballite}$$
$$3(Al_2O_3.SiO_2) \rightarrow 3Al_2O_3.2SiO_2+SiO_2$$

The silica formed during this thermal transformation partially react with impurities mainly alkalis and iron oxide to form a liquid phase and finally a vitreous silicate phase which impairs the quality of product by deteriorating the high temperature properties like hot MOR, thermal shock resistance of the products. The silica rich glass contains 1-3% Fe_2O_3, 1-3% K_2O and other alkalis oxide. Complete transformation lead to about 80% mullite and 20% glass. Formation of a liquid phase promotes atomic diffusion and allows mullitization to occur through a dissolution- diffusion-precipitation (SDP) mechanism. Mullitization starts in inclusion rich-zones and reaction rims grow from the surface of the grain as well as from cracks or perturbed zones. The decomposition details of kyanite group minerals and mullite are summarized in Table 1. The purpose of this paper is to investigate the role of the temperature, time and size of particles on the kinetics of mullitization and densification of kyanite concentrate obtained by ore-dressing Mishidowan- Bafgh deposits.

Table 1. Decomposition details of kyanite group minerals and mullite

Characteristics	Kyanite	Andalusite	Silimanite	Mullite
Crystalline system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
ρ(gr/cm3)	3.53-3.65	3.13-3.16	3.23-3.27	3.06-3.15
$T_{decomposition}$	1410	1500	1625	-
%ΔV	15	4	8	-
Silica form	Crystoballite	amorphous	amorphous	-

2. EXPERIMENTAL PROCEDURE

The used raw materials obtained by ore-dressing the Mishidowan-Bafgh kyanite deposits (Fig. 1) [1].

To enhance the reaction sintering, all the bathes were attrition-milled in water medium by using of alumina balls for a specified time period in a Fast-Mill. Obtained slurries were dried at 110°C, powdered to break the agglomerate, mixed with organic binder and uniaxially pressed at 80 MPa. The green samples after drying were fired in an electric furnace with the heating rate of 5 °C/min up to 1100 °C and of 3 °C/min up to the final firing temperature. Mullitization kinetics were studied for temperature ranging from 1400-1600 °C and soaking time from 1-3h for several concentrates of kyanite with mean dimensions 38,150 and 300 μm. Fired samples were characterized in terms of bulk density, hardness, microstructure phase assembly and thermal shock resistance. Bulk density and apparent porosity of the green as well as sintered product were determined by using of Archimedes principle in xylene and water medium respectively. XRF analyses X-ray powder diffraction pattern of the raw materials and fired products were obtained in an X-ray diffractometer (40 KV, 38mA) using nickel filtered Co (λ=1.79A?) radiation. Diffraction pattern were recorded for the 2θ range 0-70. The amount of mullite for each sintered sample is determined by X-ray quantitative analysis by using of a reference pure 3/2- mullite. The picks with highest intensity ({210}, 2θ=26.267, d=3.38°A) for the studied sample was compared with the equivalent pick for reference sample. The rate of mullitization for each sintered sample is computed by dividing X-ray quantitative analysis to the maximum mullite concerning complete mulltization sample.

The complete mullitization samples were submitted to thermal shock in air. The large well –formed samples were cut to obtain square slabs

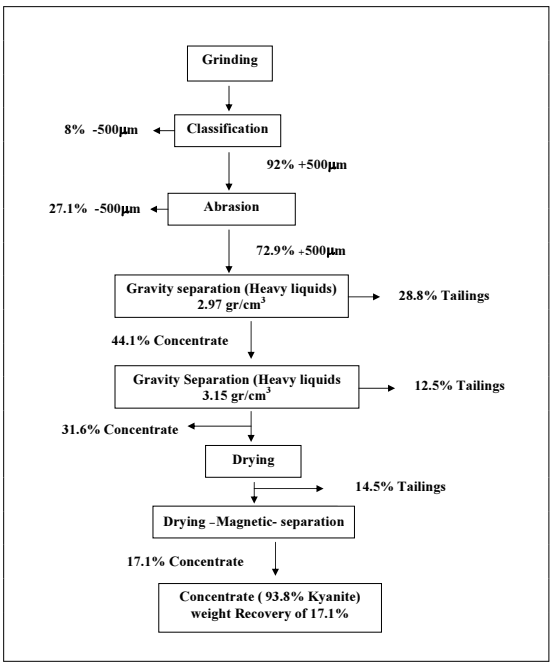


Fig.1. A flow-sheet of mineral processing for Mishidowan-Bafgh kyanite deposits

(6x6x3 mm3) and one face was polished. Each sample was rapidly extracted from the furnace and placed on a cooled water container after temperature stabilization about 10 min at 1200°C. After using sputtered gold coating on the polish surface of the sintered samples, heated (1300-1500 °C during 30-60 min) and chemical (solution 10% HF during 30s) etching, microstructure analysis were carried out by scanning electron microscopy (SEM, Philips XL30).

3. RESULTS AND DISCUSSION

3. 1. Raw Materials Characterization

The quantitative mineral composition of the concentrate may be evaluated from their chemical composition (Table 2) and XRD Pattern (Figure 2) by a calculation similar to that for the petrological norm of a rock. The calculation reveal that the concentrate contains mostly 88% kyanite associated with small amount of corundum aggregate (?4%) and 8% muscovite mineral as impurities. Usually, the pick of related phases will not appear for phases less than 5% in pattern of XRD diffraction. Such phases can be detected with the high sensitivity XRD system (Table 3). Although in such system, there is a higher error for quantitative amount of phases

The microscopic observation under polarizing microscope shows the dispersion of kyanite, silimanite, chyastolite, andalusite and corundum crystals in kyanite concentrate (Figure.3).

Table 3. Mineralogical analysis of kyanite concentrate with high sensitivity XRD system

%	Mineral
67.8	Kyanite: $Al_2O_3.SiO_2$
3.9	Andalusite: $Al_2O_3.SiO_2$
11.8	Quartz: SiO_2
6.2	Albite: $Na(AlSi_3O_8$
11.5	Anortite: $Ca(Al_2Si_2O_8)$
1.5	Zinwaldite: $K(Li,Fe\ Al)_3[(OH)_2AlSi_3O_{10}]$

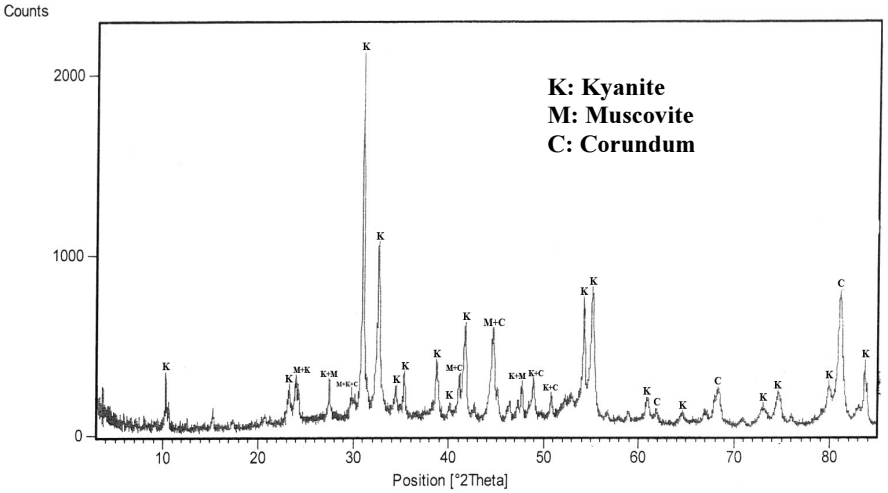
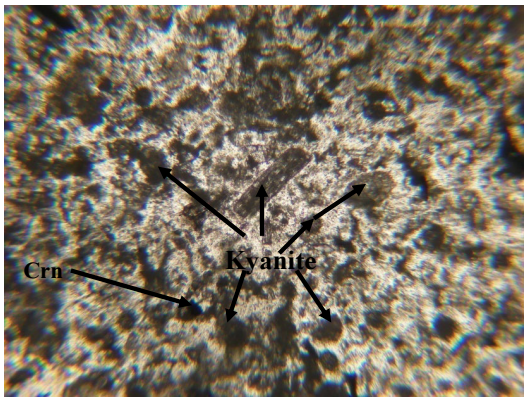


Fig. 2. XRD pattern of kyanite concentrate

Table 2. Chemical analyses (XRF) of kyanite concentrate

Composition	CaO	MgO	Na_2O	K_2O	Fe_2O_3	SiO_2	Al_2O_3
%	0.17	0.34	0.3	1.1	1.03	36.58	60.44



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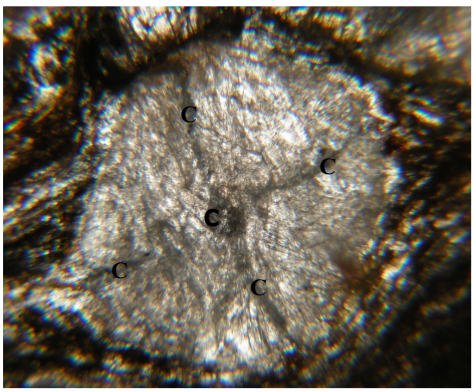

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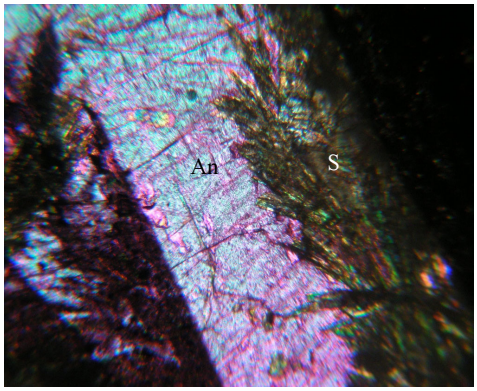

(XPL, ×100)

Fig. 3. Photomicrograph of kyanite concentrate
Crn. Corundum An: Andalusite Sil: Silimanite C: Carbon [16]

3. 2. Densification

Kyanite concentrates contains many impurities such as K_2O, Na_2O, MgO, Fe_2O_3 and small amount of corundum aggregate. Due to the chemical reaction between SiO_2 and alkali impurities liquid phase during sintering process form that aid densification by mechanism SPD. On the other hand, the thermal decomposition of kyanite into mullite leads to a volumetric expansion decreasing the densification. Thus, in sintering mechanism the chemical reaction and densification the compact (kyanite→mullite) complete each other and take place in a single step. The bulk density initially increases with soaking time and sintering temperature up to a certain level (1550°C, 2.5h) (table 4 and figure 4). Beyond this condition it decreases due to overfiring and excessive amount liquid formation. When the sample fired at higher than 1550 °C and longer time of 2.5 h bloating of surfaces and increasing of porosity were observed because of blowing and swelling of glassy phase (Figure 4). Evolution of densification for the samples with different particle size sintered in the 1550 °C isothermal

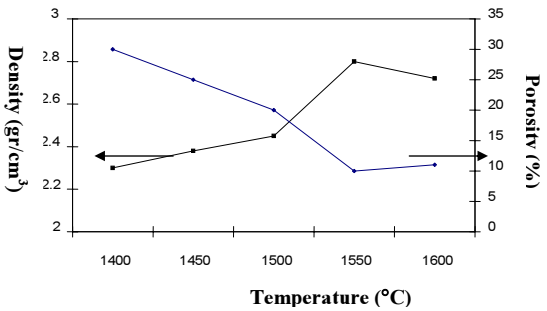

Fig. 4. Effect of sintering temperature on the bulk density and porosity of the samples

Table 4. Physical and mechanical properties of sintered samples in different conditions

T (°C)	1400	1450	1500	1550	1600	1550
t(h)	1	1	1	1……2…..2.5…..3	1	2.5
Paticle size	<38μm	<38μm	<38μm	<38 μm	<38μm	<38...<75...150..<300
$\%D_{th}$	60	75	85	92.5…93.7…95…94.6	88	95…..92……89....85
HV (Kg/mm^2)	280	300	348	428…569…630…615	650	630..580…509…430
ΔTc (°C)	250	275	298	300…336…379…361	340	379..350…365…280

treatment show that densification is higher for 38 μm particles size rather than for others (Table 4).

3. 3. Mullitization

Because of the presence of a glass phase, despite of complete mullitization (only reveal diffraction picks of 3/2 mullite on x-ray diffraction pattern) amount of mullite is lower of 100% (Table 5). The amount of mullite for complete mullitization depends on the initial kyanite content in raw materials.

Figure 5 shows the evolution of the amount of mullitization versus the soaking time at different temperatures with 38 μm in size for kyanite concentrate. At 1600 °C mullitization is very fast and complete mullitization is achieved during the first hour of soaking time. At 1550 °C complete mullitization is reached only after 2 hours. Below 1500 °C the rate of mullitization is only achieved lower than 75% after 2.5 hours. XRD patterns confirm the above results (Fig. 6a-c).

Fig 7 shows the evolution of mullitization versus the soaking time at 1550°C isothermal treatments for kyanite concentrates with different particles size. The kinetics of mullitization depends on the grain size of kyanite concentrate which it is faster for 38 μm particle size than for 150 μm ones and are slower for 300 μm . XRD patterns for 300 μm particle size sintered at 1550°C /2h shows that mullitization is not complete and the picks of silimanite detected while for 38 μm particle size at same condition of sintering mullitization was completed (Fig.6c-d). Kinetic of mullitization is always faster for the smallest kyanite grains. The results show that the only particle smaller than 150 μm seem to be affected a size effect. This is related to a higher specific surface for smaller kyanite particle size of 150 μm.

Table 5. The maximum amount of mullite for complete mullitization of the kyanite concentrates

	38 μm	150 μm	300 μm
Mullite amount for complete mullitization (%)	78.7	76.4	79.3

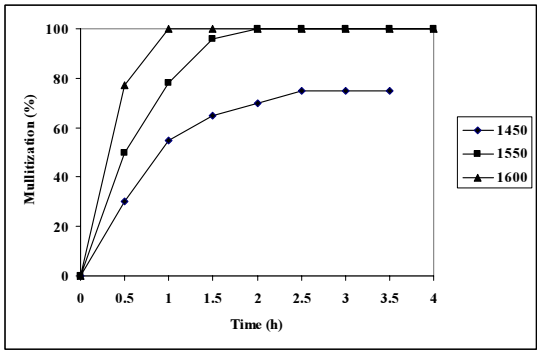

Fig. 5. Results of mullitization versus the soaking time at different temperatures with 38 μm in size for kyanite concentrate

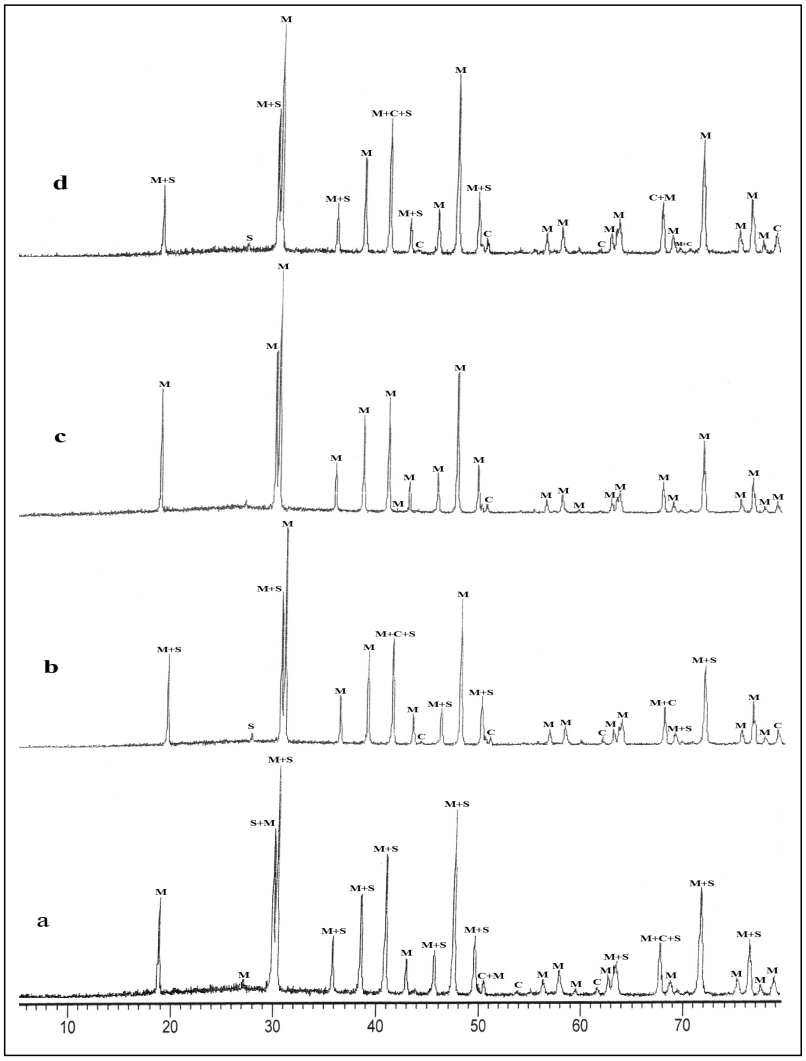

Fig. 6a-d. XRD patterns of 38 μm particle size of kyanite sintered at different temperatures during soaking time constant of 2 hours a: 1400°C b: 1500 °C c: 1550 °C and d: 300 μm - 1550°C /2 h
M: Mullite Sil: Silimanite Crn: Corundum [16]

3. 3. Microstructure

After firing the sample at 1400◦C /2h shows the existence of large mullite crystals with higher aspect ratio (needle-like) corresponding to primary mullite grown in a glassy matrix (Fig 8a). At higher temperature and longer soaking time (1600 ◦C/2.5h) smaller secondary mullite crystals nucleated from the transitory liquid by the dissolution of alumina (Fig. 8b). Also at this temperature the residual corundum was appreciably less as was also evidenced by XRD analysed (Figure 6a-c). Presence of corundum

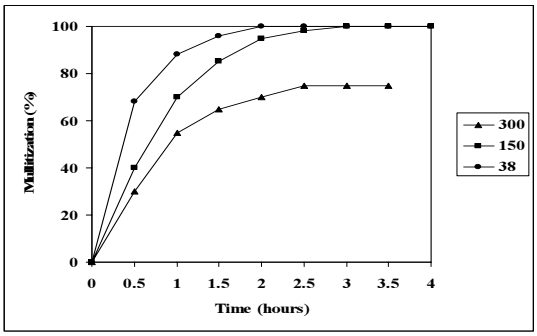

Fig. 7. Evolution of mullitization versus the soaking time at 1550 °C/2h isothermal treatment for kyanite concentrates with different particles size

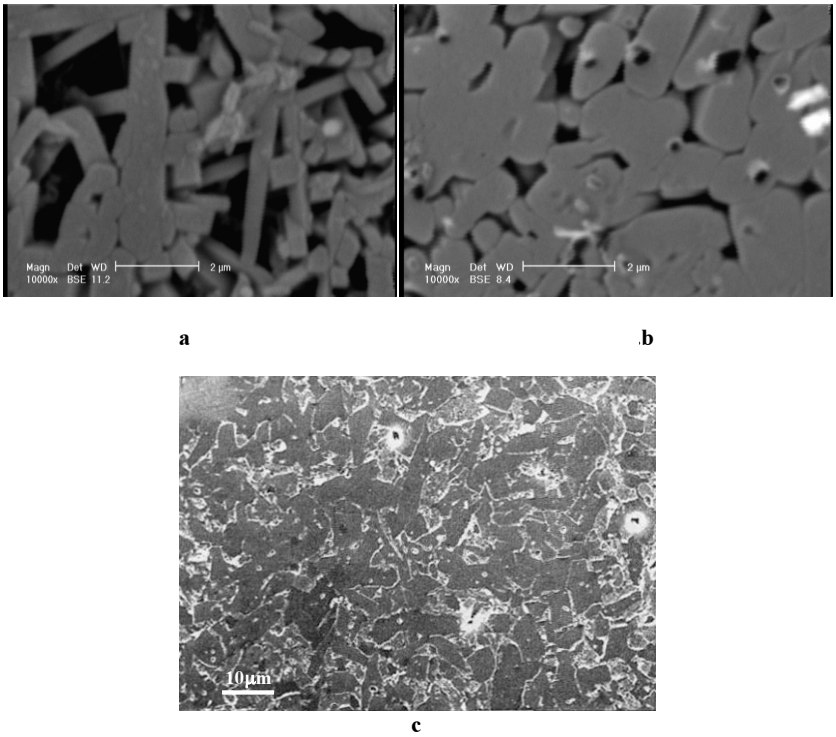

Fig. 8. SEM microstructure of sample sintered at different condition of a: 1400°C/2h, b: 1600°C /2.5h and c: 1550°C /2.5h

into the initial kyanite concentrate (Fig. 2a) reduces the silicate phase as results of mullite formation. After firing at 1550 °C/2.5h the grain morphology appeared to be a mixture of equiaxed secondary mullite crystal and lath-like primary mullite crystal grown with a large aspect ratio (Figure 8c). The black voids in the micrograph 8a,b are due to the dissolution of the silicate phase in HF during chemical leaching. The mullitized sample exhibits a typical behavior of composites materials (mullite – glass). The presence of a liquid phase lead to heal initial cracks of the andalusite grains during the mulitization, then, the composite mullite – glass appears uncracked. Microcrackes are defected and stopped in glass zones. Therefore, the specific microstructure of mullitized kyanite leads to excellent thermal shock resistance in comparison with monolithic mullite (without glassy phase). They are well suited for a thermal cycling use. These results offer a new possibility for the development of refractories with optimized microstructure by using of kyanite raw materials.

4. CONCLUSION

By firing compact kyanite concentrate powder obtained by ore-dressing of Mishidowan andalosite deposits, a 3Al2O3.2SiO2 mullite was formed by a dissolution–precipitation mechanism. This mechanism involving silica rich liquid issued by low temperature melting of impurities results a composites containing the equiaxe and needle-like grains of mullite with a capillary network filled with silica rich glass. Kinetic of mullitization depends on the originion, particle size and conditions of sintering of the kyanite concentrate. Highest densification take place at 1550°C/2.5h and complete mullitization is reached at 1550?C/2h. Kinetics of mullitization are always faster for the smallest kyanite grains, as the results show that only particles smaller than 150?m seem to be affected by size effect.

5. ACKNOWLEDGEMENT

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