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STRUKTURA KERAMIČKOGA MATERIJALA

THE STRUCTURE OF CERAMIC MATERIALS

Pregledni članak / Review paper

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U arheologiji je keramika najčešći pokretni materijal koji se pronalazi prilikom istraživanja. Pri njezinoj obradi važno je poznavati strukturu keramičkih materijala. Varijacije u strukturi javljaju se zbog kemijskih svojstava same gline, primjesa u glini te razlika u procesu pečenja. U radu se iznose podaci o primjesama koje se prirodno nalaze u glini i onima koje joj se naknadno dodaju, a važne su zbog funkcionalnih karakteristika kao što su temperaturna otpornost, porozitet i, ponajprije, boja i čvrstoća pečenoga proizvoda. Varijacije u strukturi keramičkoga materijala javljaju se i zbog razlika u procesu pečenja koji podrazumijeva vrijeme pečenja, temperaturu i atmosferu tijekom gorenja i hlađenja. Promjene koje nastaju pri pečenju (na otvorenome ognjištu ili u zatvorenoj peći) uključuju: isparavanje, termičko raspadanje glinenih minerala i sinteriranje, vitrifikaciju te hlađenje i pražnjenje peći.

Za istraživanje strukture keramičkoga materijala koriste se razne metode. Njima se nastoji utvrditi sastav glinene smjese i postoci raznih primjesa te opisati kemijski procesi koji nastaju prilikom pečenja.

Ključne riječi: struktura keramičkoga materijala, keramika, glina, primjese, pečenje

In archaeology, ceramics are the most common movable materials discovered during the course of excavations. Knowledge of the structure of ceramic materials is vital to its analysis. Variations in structure appear due to the chemical properties of the clay itself, additives in the clay and differences in the firing process. This work presents data on additives naturally found in clay and those subsequently added, and these are important due to functional features such as resistance to temperature extremes, porosity and, above all, the colour and tenacity of the fired product. Variations in the structure of ceramic materials also appear due to differences in the firing process, which implies firing duration, temperature and atmosphere during heating and cooling. Changes which emerge during firing (in open hearths or in closed kilns) include: evaporation, thermal decomposition of clay materials and sintering, vitrification and cooling and emptying of kilns.

Various methods are used to study the structure of ceramic materials. They are used in an attempt to ascertain the composition of the clay and percentages of different additives and to describe the chemical processes that occur during firing.

Key words: structure of ceramic materials, ceramics, clay, additives, firing

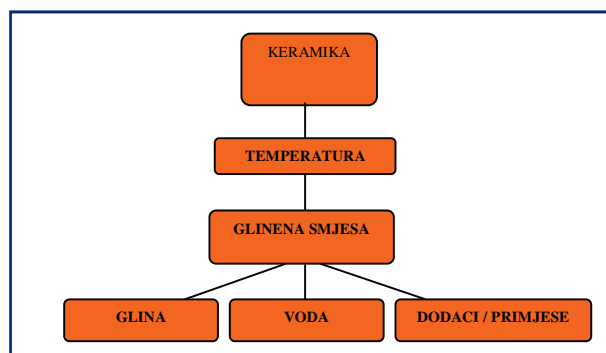
UVOD

Pojava lončarstva i uporaba keramičkih predmeta predstavljaju veliku prekretnicu u razvoju čovječanstva. Od neolitika nadalje keramički predmeti postaju dio svakodnevnice svih naroda i stoga su jedan od glavnih čimbenika za ekonomsku i kulturnu determinaciju određenoga razdoblja i prostora. U arheologiji keramika je najčešći pokretni materijal nađen prilikom istraživanja. Za njenu obradu važno je, osim tehnologije, poznavati strukturu keramičkih materijala. Na taj se način osim tipološko-kronoloških analiza može bolje razumjeti tehnika izrade keramičkih predmeta, a samim time i način njihove uporabe.

Struktura keramičkoga materijala može se analizirati *makroskopski* (taktilno, vizualno, mehaničkim testovima – skalpelom) i *mikroskopski* (spektrometrom *X-ray*, raznim laboratorijskim analizama, specijaliziranim mikroskopima, petrolozijskim analizama).

Riječ ‘keramika’ dolazi od grčke riječi *keramos*, što znači glina, dok se riječju *keramikos* (keramički, lončarski) opisuje pečeni proizvod, a ne sirovinski materijal (grč. *keramike tekhnē* označava keramičku vještinu, lončarstvo).

U kemiji keramika predstavlja anorganski materijal nastao iz gline koja se u dodiru s vodom pretvara u smjesu za oblikovanje, a pri izlaganju toplini formira se u kompaktni keramički materijal. Struktura keramičkoga materijala razlikuje se od predmeta do predmeta. Varijacije se javljaju zbog kemijskih svojstava gline, nečistoća odnosno primjesa u glini te razlika u procesu pečenja (sl. 1) (Shepard 1985: 6–48; Horvat 1999: 15–16).



Slika 1. Grafički prikaz nastajanja keramike (autor: I. Miletić, 2007).

GLINA KAO OSNOVNA SIROVINA ZA IZRADU KERAMIKE

Glina je vrsta sedimentnoga tla nastala raspadanjem magmatskih stijena pod utjecajem atmosferilija. Od svih sedimentnih stijena na Zemlji 70% njih gline su tla. Gline se sastoje od sitnih čestica alumi-

INTRODUCTION

The appearance of pottery and the use of ceramics constituted a great watershed in the development of humankind. From the Neolithic onward, ceramics became a part of the everyday lives of all peoples and thus one of the principal economic and cultural determinants of a specific era and place. In archaeology, ceramics are the most common movable materials found during the course of research. In addition to the relevant technology, knowledge of the structure of ceramic materials is important to its analysis. In this manner, besides typological-chronological analysis, one can better understand the techniques used to make ceramic items and, by extension, how they were used.

The structure of ceramic materials can be analysed *macroscopically* (tactilely, visually, mechanical tests – e.g. using a scalpel) and *microscopically* (*X-ray* spectrometer, various laboratory analyses, specialised microscopes, petrological analysis).

The word ‘ceramic’ comes from the Greek word *keramos*, which means (potter’s) clay, while the word *keramikos* (ceramic, potter’s) describes the fired product rather than the raw material (the Greek *keramike tekhnē* designates the ceramic craft, pottery).

In chemical terms, ceramic is an inorganic material made of clay which, in combination with water, turns into a malleable compound, and when exposed to heat it becomes a compact ceramic material. The structure of ceramic materials varies from item to item. Variations appear due to the chemical properties of the clay, impurities or additives in the clay and differences in firing processes (Fig. 1) (Shepard 1985: 6–48; Horvat 1999: 15–16).

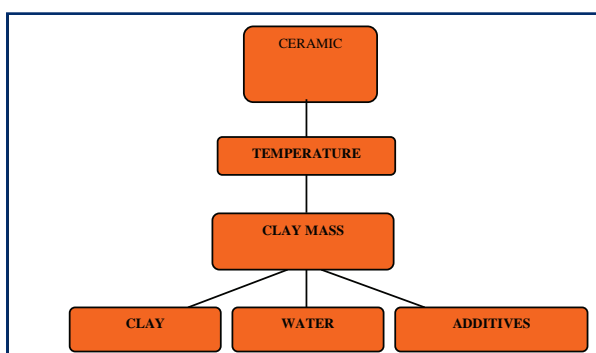


Figure 1. Graphic depiction of ceramic production (author: I. Miletić, 2007).

CLAY AS THE BASIC RAW MATERIAL TO MAKE CERAMIC

Clay is a type of sedimentary earth that emerges after magmatic rock is worn by weathering. Out of all of the sedimentary rocks on the planet, 70% is clay. Clays are composed of fine-grained alumin-

nosilikata¹ (kaolinita, montmorillonita, ilita, klorita, nontronita, halozita, alofona i dr.) i raznih primjesa: kremena, raznih željeznih, kalcijevih i drugih spojeva, humusa i ugljevite materije (Barić & Tajder 1967: 207; *Opća enciklopedija* 3, 1977: 182–183).

U prirodi razlikujemo *čiste* gline (bijeke su ili sivkaste boje) i *nečiste* gline (žute su boje one od limonita, crvene od hematita, zelenkaste od glaukonita te tamnosive i crne od ugljevitih materija). Čiste se gline bez primjesa nazivaju *masne*, a one s mnogo primjesa *posne* gline.

Masne se gline, glatke i sjajne površine, odlikuju velikom plastičnošću. Mogu upiti znatne količine vode i imaju veliku vezivnu moć. Posne gline imaju suprotne osobine: hrapavu površinu, pjeskovite su i lako se otapaju u vodi. Za izradu keramike koriste se obje vrste gline, ovisno o namjeni i tehnologiji izrade (Šimić-Kanaet 1990: 83–84).

Gline prema nalazištima dijelimo na *primarne* i *sekundarne*. Primarne su gline ostale na mjestu nastanka ili su se malo pomicale. Sadrže malo primjesa i mogu se peći na visokim temperaturama. Primarne se gline ne moraju doradivati ako se koriste za izradu keramike. Najvažnije su primarne gline *kaolini* (porculanska glina); najčistiji su oblik gline i sadrže vrlo malo ili nimalo primjesa. Svi su kaolini vatrostalni, a tope se na temperaturi višoj od 1600 °C (Verigo 1960: 25). Sekundarne su se gline pomicale pod utjecajem vode, erozije ili vjetrova. U transportu mijenjale su sastav i osobine. Taloženjem u vodi postale su plastičnije zbog raznih minerala koje sadrže. Neke su sekundarne gline previše plastične za oblikovanje i pucaju tijekom pečenja ili sušenja. Zbog tih karakteristika njima se dodaju neplastične primjese (aditivi). To mogu biti minerali (kvarc – SiO₂, kalcit – CaCO₃), organski materijal (biljke, korijenje, sjemenje), biominerali (školjke, koralji) ili samljevena keramika (grog) (Rye 1988: 29–31).

Najpoznatija je sekundarna glina ilovača. Zbog svoje je rasprostranjenosti, kemijskoga sastava (različite primjese minerala, aluminosilikati, kvarc i pijesak) i niskoga tališta oduvijek bila najpogodnija za izradu keramike (Rice 1987: 37).

Plastičnost i čvrstoća pri izlaganju toplini dva su svojstva gline najvažnija za izradu keramike. Plastičnost je sposobnost gline da natopljena određenom količinom vode i nakon modeliranja zadrži oblik. Stupanj plastičnosti ovisi o veličini i količini

silicates¹ (kaolinite, montmorillonite, illite, chlorite, nontronite, halloysite, allophane, etc.) and various compounds: flint, various iron, calcium and other compounds, hummus and coal-like substances (Barić & Tajder 1967: 207; *Opća enciklopedija* 3, 1977: 182–183).

In nature, a distinction is drawn between *pure* clay (white or greyish) and *impure* clay (yellow for limonite, red for haematite, greenish for glauconite and dark grey and black for coal-like substances). Pure clays without additives are called *greasy*, while those with many additives are called *frugal* clays.

Greasy clays, with smooth and shiny surfaces, are characterised by a high degree of plasticity. They can absorb a considerable quantity of water and they have great bonding properties. Frugal clays have the opposite qualities: they have coarse surfaces, are sandy and easily dissolve in water. Both types of clay are used to make ceramic, depending on the purpose and production technology (Šimić-Kanaet 1990: 83–84).

Based on their deposit sites, clays are classified as *primary* and *secondary*. Primary clays remain at their place of origin or move slightly. They contain few additives and they can be fired at high temperatures. Primary clays must be additionally processed if they are to be used to make ceramic. The most important primary clays are *kaolins* (porcelain clay): the purest form of clay containing very little or no additives. All kaolins are refractory, and they melt at temperatures higher than 1600°C (Verigo 1960: 25). Secondary clays have been moved by water, erosion or wind. Their composition and qualities are altered by such movement. Sedimentation in water makes them more plastic due to the various minerals they contain. Some secondary clays are too plastic to be formed and crack during firing or drying. Because of these characteristics, non-plastic additives are added to them. These may be minerals (quartz – SiO₂, calcite – CaCO₃), organic materials (plants, roots, seeds), bio-minerals (shells, coral) or pulverised ceramic (grog) (Rye 1988: 29–31).

The best known secondary clay is loam. Its wide distribution, chemical composition (various mineral compounds, aluminosilicates, quartz and sand) and low melting point has always made it the most suitable for making ceramic (Rice 1987: 37).

¹ Aluminosilikati (feldšpati, glinenci) pripadaju skupini silikatnih minerala. Nisu stabilni, pa djelovanjem vode i atmosferijala prelaze u glinu. U aluminosilikate ubrajamo vapno, sodu, potašu itd. Koriste se kao topitelji. Većina ih ima relativno visoku točku topljenja: potaša 1150 °C, soda 1118 °C, vapno 1550 °C, ali ta se temperatura može sniziti dodatkom drugih aluminosilikata ili vapnenca (CaCO₃) i kvarca (SiO₂) (Rice 1987: 96–98).

¹ Aluminosilicates (feldspars, clay minerals) belong to the silicate mineral group. They are not stable, so they turn to clay when exposed to water and weathering. Aluminosilicates include lime, soda, potash, etc. They are used as solvents. Most of them have a relatively high melting point: potash – 1150°C, soda – 1118°C, lime – 1550°C, but these temperatures may be lowered by adding other aluminosilicates or limestone (CaCO₃) and quartz (SiO₂) (Rice 1987: 96–98).

ni glinenih zrna te o sastavu primjesa (Scott 1958: 379). Čvrstoća pri izlaganju toplini drugo je važno svojstvo gline. Nakon sušenja, u procesu pečenja, ispari sva preostala voda iz oblikovane glinene smjese. U tom se procesu promijeni mineralna struktura te nastaje keramika i taj je proces nepovratan (Rice 1987: 80).

PRIRODNE ILI UMJETNO DODANE PRIMJESE U GLINI

Primjese se u glini već nalaze ili se naknadno dodaju i mijenjaju svojstva smjese za izradu keramike. Važne su zbog funkcionalnih karakteristika kao što su temperaturna otpornost, porozitet i, ponajprije, boja i čvrstoća pečenoga proizvoda (Rice 1987: 93–96).

Primjese možemo podijeliti u tri skupine.

A. Štetne primjese koje se prirodno nalaze u glini, odnosno u glinenoj smjesi. Gline se mogu koristiti u obliku u kakvu se nalaze u prirodi, bez modifikacija. No češće gline se oblikuju da bi bile pogodnije za uporabu, i to tako da se uklanja nečistoća i/ili dodaju primjese u nju. Uklanjanje nečistoća podrazumijeva uklanjanje štetnih primjesa iz sirove gline koje bi nepovoljno utjecale na gotov keramički proizvod. Takve se primjese uklanjaju ručno, prilikom sušenja gline, drobljenjem, prosijavanjem ili ispiranjem gline razrijeđene vodom. Glineni materijal treba očistiti od krupnih komada drveta, bilja, viška ostalog organskog materijala, većih komada minerala, viška pijeska i soli, vapna, sadre i kamenčića. U glini su osobito štetna krupnija zrna vapnenca. Pri pečenju iznad 700 °C vapnenac (CaCO_3) prelazi u živo vapno (CaO) koje nakuplja vlagu i tako povećava volumen stijenki ($\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$). Takva se keramika u dodiru s vodom raspada. Zato se vapnenac mora reducirati ili valja sniziti temperaturu pečenja (Rice 1987: 118).

B. Primjese kojima se mijenja svojstvo smjese da bi se postigla stabilnost, spriječila poroznost, uravnotežio gubitak mase pri sušenju, postigla otpornost na temperaturne promjene itd. U prirodne ili umjetno dodane primjese ubrajamo: kvarc (SiO_2), kalcijev karbonat (CaCO_3), organske primjese, samljevenu keramiku, grafit, tinjac te druge primjese. Njima se nastoji promijeniti svojstvo smjese kako bi se postigla stabilnost, spriječila poroznost, uravnotežio gubitak mase pri sušenju te postigla otpornost na temperaturne promjene.

Kvarc (SiO_2) je mineral jedne od kristalnih modifikacija silicij-dioksida (SiO_2 , silika). U prirodi se javlja u obliku gorskoga kristala, kvarcnoga pijeska, kvarcita, ametista, kremena i u raznim drugim obli-

Plasticity and tenacity when exposed to heat are the clay properties most important to ceramic production. Plasticity denotes the quality of clay which allows it to absorb a specific amount of water and retain its form after modelling. The degree of plasticity depends on the size and quantity of clay grains in the additive composition (Scott 1958: 379). Tenacity when exposed to heat is the other vital property of clay. After drying, during the firing process, all remaining water evaporates from the modelled clay mixture. During this process, otherwise irreversible, the mineral structure changes and ceramic is created (Rice 1987: 80).

NATURAL OR ARTIFICIAL ADDITIVES IN CLAY

Additives can already be in the clay or added later; they change the properties of the mass for making ceramic. They are important due to their functional characteristics such as heat resistance, porosity, and, primarily, colour and tenacity of the fired product (Rice 1987: 93–96).

Additives can be classified into three groups.

A. Harmful additives naturally found in clay or the clay mass. Clays can be used in the condition in which they are found in nature, without modification. But more often clays are formed to be more suitable for use, usually by removing impurities and/or blending in new additives. The removal of impurities implies removal of harmful additives from the raw clay which may unfavourably influence the finished ceramic product. Such additives are removed manually, when the clay is dried, by pulverising, sifting or washing the clay thinned with water. Large pieces of wood, plants, other excess organic materials, larger mineral pieces, excess sand and salt, lime, gypsum and pebbles need to be removed from the clay materials. Larger limestone grains are particularly harmful to clay. When fired at temperatures exceeding 700°C, limestone (CaCO_3) turns to quicklime (CaO) which gathers moisture and thus increases the volume of the walls of the ceramic item ($\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$). Such ceramic falls apart in contact with water. This is why limestone must be reduced or the firing temperature lowered (Rice 1987: 118).

B. Additives which change the property of the mass to achieve stability, prevent porosity, balance the loss of mass at drying, achieve resistance to changes in temperatures, etc. Natural or artificially added additives include: quartz (SiO_2), calcium carbonate (CaCO_3), organic additives, grog, graphite, mica and other additives. These are added to change the property of

cima. Topi se na temperaturi od oko 1700 °C. Kvarc (SiO_2) je jako tvrd mineral i lomi se pregrijavanjem iznad 800 °C. U glini je koristan samo jako usitnjen ili u malim količinama. Posude s primjesom kvarca mogu se izlagati većim temperaturama i izravnoj vatri, pri čemu zrnca kvarca prenose toplinu na stijenke u posudi. Kvarc daje keramici čistu boju i veću otpornost na temperaturne promjene (Verigo 1960: 27–28; Rice 1987: 93–96).

Kalcijev karbonat (CaCO_3) u prirodi se javlja u obliku kristala kao što su vapnenac i kalcit, ali ima ga i u školjkama i u mnogim glinama. Pridonosi bržemu vezanju i čvrstoći gline. Keramika koja sadrži kalcijev karbonat (CaCO_3) peče se na temperaturama nižima od 750 °C. Iznad te temperature kalcijev karbonat (CaCO_3) prelazi u kalcijev oksid (CaO , živo vapno) koji izaziva pucanje stijenki posuda (Karšulin 1955: 286; Shepard 1985: 6–48).

Organske tvari (ugljik, ostaci biljaka, alge, bakterije) daju glinenoj smjesi tamnu boju, no u pečenju one oksidiraju i keramika dobiva svjetliju boju. Koliko kisik prodre u stijenke keramike, toliko će svijetli sloj (vanjski) biti deblji. Na mjestu kamo kisik ne dopire organske tvari karboniziraju, to jest pougljene. U strukturi keramičkih stijenki vidljivi su otisci organskih tvari koje su pri pečenju izgorjele. Te su praznine korisne u posudama za kuhanje jer prekidaju pukotine koje se javljaju kao posljedica termalnoga stresa tijekom uporabe.

Samljevena keramika (grog) umjetno je napravljena primjesa. Za izradu se može koristiti odbačena i oštećena keramika. Vrlo je pogodna zbog svoje dostupnosti, a i usitnjava se lakše od različitih stijena i minerala. Kako je ta keramika već pečena, stabilna je pri ponovnome pečenju i zadržava ista svojstva kao masa u koju se stavlja. Dodaje se glini da bi se povećala otpornost predmeta na temperaturne promjene, udarce i razne reakcije unutar strukture predmeta (Karšulin 1955: 288; Rye 1988: 31–40).

Grafit² je kristal tamnosive boje postojan pri visokim temperaturama. Kao dobar vodič topline poboljšava otpornost keramike na temperaturne promjene. Temperatura mu je topljenja 3800 °C (Verigo 1960: 31; Horvat 1999: 16).

Tinjac (mika, liskum) silikatni je mineral koji izgrađuje mnoge stijene, a kao primjesa pojačava plasticitet glinene smjese i povećava otpornost keramike na temperaturne promjene. Proces taljenja tinjca počinje na relativno niskim temperaturama, ali se on rastali tek na oko 1000 °C (Rye 1988: 31–40).

the mass to achieve stability, prevent porosity, balance the loss of mass at drying, and achieve resistance to changes in temperatures.

Quartz (SiO_2) is a mineral that is one of the crystal modifications of silicon dioxide (SiO_2 , silica). In nature it appears in the form of rock crystal, quartz sand, quartzite, amethyst, flint and in other, various forms. It melts at temperatures of approximately 1700°C. Quartz (SiO_2) is a strong, hard mineral that fractures when heated at temperatures above 800°C. In clay it is only useful in very fine-grained or small quantities. Vessels with quartz additives can be exposed to high temperatures and direct flame, and the quartz crystals transfer the heat to the walls of the vessels. Quartz gives ceramic a clear colour and greater resistance to changes in temperature (Verigo 1960: 27–28; Rice 1987: 93–96).

Calcium carbonate (CaCO_3) appears in nature as crystals such as limestone and calcite, but it can also be found in shells and in many clays. It contributes to faster bonding and the firmness of clay. Ceramic containing calcium carbonate (CaCO_3) is fired at temperatures below 750°C. Above this temperature calcium carbonate (CaCO_3) becomes calcium oxide (CaO , quicklime) which causes the vessel walls to crack (Karšulin 1955: 286; Shepard 1985: 6–48).

Organic substances (carbon, plant remains, algae, bacteria) give the clay mass a dark colour, but during firing they oxidise and the ceramic becomes lighter. The more oxygen that is absorbed into the walls of the ceramic, the thicker the lighter (external) layer. Organic substances carbonise at places not reached by oxygen. Imprints of organic substances that burn during firing are visible in the structure of the walls of the ceramic. These empty points are useful in cooking vessels because they stop fissures which appear as a result of thermal stress during use.

Finely ground ceramic (grog) is an artificially made additive. Discarded and damaged ceramic can be used to make it. It is very suitable due to its availability, and it is ground more easily than various rocks and minerals. Since the ceramic is already fired, it is stable during renewed firing and retains the same properties as the mass into which it is inserted. It is added to clay to increase its resistance to temperature changes, impact and various reactions inside the structure of the item (Karšulin 1955: 288; Rye 1988: 31–40).

Graphite² is a dark-grey crystal that remains stable at high temperatures. As a good heat conductor, it improves the resistance of ceramic to temperature

² Nalazišta grafita u nas su malena i rijetka, a najviše ga ima kod Pakraca i na Psunju.

² Graphite deposits in Croatia are small and rare; most can be found at Pakrac and on the slopes of Psunj.

Kvarc i pijesak dodaju se primarnoj glini zbog postojanosti u vatri (podnose nagle promjene temperature), što je važno npr. za kuhinjsko posuđe i grubu keramiku.

Gline koje sadrže pijesak ili im se on dodaje u određenome omjeru peku se na nižim temperaturama. Količina pijeska važna je pri određivanju načina pečenja; npr. keramika pečena u ognjištu sadrži više pijeska i peče se na nižoj temperaturi od keramike pečene u klasičnoj peći (Šimić-Kanaet 1990: 82).

Smjesa kalcitnoga kamena, pijeska i kamene prašine ili pečenih školjaka, tzv. 'vrsta', dodaje se glini da bi se poboljšala kvaliteta glinene smjese. 'Vrsta' u glini mora biti ravnomjerno raspoređena u točno određenome omjeru. Ako je 'vrste' manje, posude pri pečenju pucaju, a ako je 'vrste' previše, posuda umočena u vodu nakon nekog se vremena raspadne u prah (Kalmeta 1954: 127–168).

Bazalt u glinenoj smjesi može proizvesti vrlo tvrdu keramiku već na temperaturi od 1000 °C. Bazalt je eruptivna površinska stijena tamne boje. Vrlo je otporna na kiseline.³

U glini mogu biti prisutne i lužine. Lužine su baze (oksidi metala i hidroksidi) topive u vodi. Gline koje sadrže lužine nazivaju se *geopolimerničke* gline. Peku se brže, bolje i na nižoj temperaturi. U proizvodnji keramike upotrebljava se natrijev bikarbonat (NaHCO_3), odnosno soda, bijeli kristalni prah koji se otapa u vodi i tvori lužnatu otopinu. Lužina, to jest soda, u prirodi se javlja kako mineral u sodnim jezerima Egipta, Turske, Sjeverne i Južne Amerike, a u sušnim krajevima mjestimice 'cvjeta' iz tla. Umjesto sode iz prirode kao lužina se može koristiti fini dio pepela koji nastaje spaljivanjem morskih alga ili pepeo nekih kopnenih biljaka (trske, duda, hrasta, bukve i paprati) (Henderson 1989: 217–229). Od kopnenih biljaka koje su lužnate posebno se ističe biljka roda *salicornia* (Ridge 2002: 206–207). Toj skupini pripadaju biljke kao što su slanjača, caklenjača, kanfranka itd.⁴ (Topić *et al.* 2006). Lužina

³ U Hrvatskoj bazalta ima u malim količinama na Lončarskome visu (*Opća enciklopedija* 1, 1977: 452).

⁴ Biljke roda *salicornia* rastu na niskoj, muljevitoj i jako vlažnoj morskoj obali, na tlu bazične (alkalične) reakcije bogatom kuhinjskom soli i karbonatima. Toj vrsti pripada zeljasta caklenjača, grmolika caklenjača, trava slanuša i druge slanuše. U Hrvatskoj se javljaju duž obale u Primorju te duž jadranske obale. U kontinentalnome području u zaslanjenim se tlima javljaju vegetacije panonskih slatina. Za sušnoga se razdoblja godine u takvu tlu voda kapilarama uzdiže do površine odakle hlapi, a izlučuje se sol koja 'iscvjetava' na površinu tla. Samo u najistočnijim dijelovima Hrvatske, u Vukovarsko-srijemskoj županiji, ima neznatnih površina s takvom zemljom. Takva su staništa uništena zbog izgradnje kanala, a slatine su pretvorene u oranice. Danas je poznata jedna takva površina u zaleđu naselja Trpinje u okolici Vukovara. Na tim tlima raste biljka jednogodišnja kafranka, kao i sitnocvijeti traputac i panonska zvijezda (Topić *et al.* 2006).

changes. Its melting point is 3800°C (Verigo 1960: 31; Horvat 1999: 16).

Mica is a silicate that forms many rocks, and as an additive it enhances the plasticity of the clay and increases the resistance of the ceramic to temperature changes. The process of melting mica begins at relatively low temperatures, but it only melts at temperatures of approximately 1000°C (Rye 1988: 31–40).

Quartz and sand are added to primary clay to ensure its stability over flames (they withstand sudden changes in temperature), which is important for, e.g. kitchenware and coarse ceramics.

Clays containing sand or with sand added in specific quantities are fired at low temperatures. The quantity of sand is important to determine the firing method; e.g. ceramic fired in a hearth contains more sand and is fired at lower temperatures than ceramic fired in a classic kiln (Šimić-Kanaet 1990: 82).

A mixture of calcite stone, sand and stone dust or fired shells is added to the clay to improve the quality of the clay mass (in Croatian this mixture is called the 'vrsta'). This additive must be in clay equally distributed in a precisely specified ratio. If there is less, the vessels crack during firing, but if there is too much, the vessel will crumble if soaked in water too long (Kalmeta 1954: 127–168).

Basalt in the clay mass can produce very hard ceramic already at temperatures of 1000°C. Basalt is a dark igneous surface rock. It is very resistant to acid.³

Alkalis may also be present in clay. Alkalis are bases (metal oxides and hydroxides) soluble in water. Clays containing alkalis are called *geopolymer* clays. They fire faster, better and at lower temperatures. Sodium bicarbonate (NaHCO_3), a white crystal powder that dissolves in water and forms an alkaline solution, is used in ceramic production. This base, also called soda, appears in nature as a mineral in soda lakes in Egypt, Turkey, North and South America, and in arid regions it "sprouts" from the ground. Besides natural soda as an alkali, the fine portion of ash that emerges after burning of marine algae, or the ash of certain terrestrial plants (reed, mulberry, oak, beech and fern) can also be used (Henderson 1989: 217–229). Among the particularly alkaline terrestrial plants are those of the genus *Salicornia* (Ridge 2002: 206–207). This group includes plants such as several local species of glasswort, saltwort

³ There are small quantities of basalt in Croatia at Lončarski vis (*Opća enciklopedija* 1, 1977: 452).

omogućuje da se svi minerali izluče prema površini predmeta i pritom mu daju metalni sjaj. Geopolimerničke gline pri temperaturi od 400 °C u oksidacijskim uvjetima pečenja proizvode keramiku crne površine i sive jezgre. Daljnjim zagrijavanjem na 600 °C jezgra keramike poprima boju mesa, a na 800 °C površina postaje ružičasta. Na temperaturi višoj od 950 °C lužnata keramika postaje žuta.

Mehanička snaga geopolimerničkih glina pečenih do 600 °C odgovara glinama bez lužina pečenim na 950–1000 °C (Boutterin & Davidovits 1982: 213–217).

Oksid dodan smjesi	Boja nakon pečenja
jarosit	ružičasta
hematit	crvena
manganovi spojevi	smeđa
grafit, manganovi spojevi	crna
svijetle gline i kobaltovi spojevi	plava
svijetle gline, kaolin	bijela

Tablica 1. Boje koje nastaju pri oksidacijskome pečenju metalnih oksida dodanih smjesi za slikanje (Horvat 1999: 42–43).

Oxide added to clay	Colour after firing
jarosite	pink
haematite	red
manganese compounds	brown
graphite, manganese compounds	black
light clays and cobalt compounds	blue
light clays, kaolin	white

Table 1. Colours which emerge during oxidation firing of metal oxides added to decoration compounds (Horvat 1999: 42–43).

C. *Primjese koje se koriste da bi se postigla estetska kvaliteta gotovoga keramičkog proizvoda, npr. određena boja ili glazura.* Posebna su kategorija primjese koje se dodaju sirovoj glini ili se nanose na gotov keramički predmet da bi se postigao željeni koloristički efekt. Na površinu keramičkoga predmeta nanose se smjese – premazi kojima se povećava otpornost i trajnost toga predmeta, ali se istodobno njima ukrašava površina predmeta. Glineni premazi (engoba, firnis – svijetli premaz, grafitni premaz⁵)

⁵ Engoba je vrsta glinenoga premaza koji se aplicira na već pečenu keramiku. Riječ je o tankome premazu bijele ili obojene glinene smjese koji nakon pečenja postiže drugu boju (bijela ili obojana engoba). Sadrži točno određene sastojke kojima se osigurava minimalan gubitak volumena posude i dobro stanje stijenki posuda (Horvat 1999: 212).

and others (*Halogeton sativus*, *Camphorosma monospeliaca*, etc).⁴ (Topić *et al.* 2006). Alkalis extract all minerals to the surface of an item, giving it a metallic sheen in the process. Geopolymer clays at temperatures of 400°C under oxidation conditions during firing produce ceramic with a black surface and grey core. Further heating at 600°C gives the core ceramic the colour of meat, while at 800°C the surface becomes pink. At temperatures higher than 950°C alkaline ceramic becomes yellow.

The mechanical strength of geopolymer clay fired at 600°C corresponds to clays without alkalis fired at 950–1000°C (Boutterin & Davidovits 1982: 213–217).

C. *Additives used to achieve aesthetic qualities in the finished ceramic product, e.g. specific colours or glazes.* A special category includes additives added to raw clay or applied to the finished ceramic product to attain the desired colour effect. Compounds/coatings are applied to the surface of ceramic items to increase their tenacity and durability while simultaneously decorating the surface.

Clay slips (*engobe*, varnish – light slip, graphite slip⁵) are applied to both fired and unfired surfaces, while glazes are only applied to fired surfaces. For painting, compounds of coloured materials are used which produce a specific colour or several colours. The nuances and intensity of the colours themselves depends on the chemical composition of the walls of the ceramic to which

⁴ Plants of genus *Salicornia* grow on low, muddy and very wet seashores, on base (alkaline) reactive soil rich in table salt and carbonates. Several species of glasswort and saltwort belong to this species. In Croatia they grow all along the coast of its Northern Littoral and on the Adriatic coast. In the continental region they appear as vegetation in the saline soils of the Pannonian salt flats. During the dry seasons, water raises to the surface in capillaries, where it evaporates, and excretes salt which “blooms” on the soil’s surface. Negligible surfaces with such soil only exist in the easternmost parts of Croatia, in Vukovar-Srijem County. Such habitats have been destroyed due to canal construction, and the salt flats have been transformed into plough fields. Today only one such surface is known in the vicinity of the village of Trpinja near Vukovar. A local perennial *Camphorosma (kafranka)*, a fine-leaved species of plantain (*Plantago*) and the ‘Pannonian star’ (*panonska zvijezda*) grow on these soils (Topić *et al.* 2006).

⁵ *Engobe* is a type of clay slip applied to larger fired ceramics. This is a thin, white or coloured clay slip which turns a different colour after firing (white or coloured *engobe*). Its contents are precisely specified, and they ensure minimum loss of volume of the vessel and the soundness of its walls (Horvat 1999: 212).

nanose se na nepečenu i pečenu površinu, a glazure samo na pečenu površinu. Za slikanje se upotrebljavaju smjese obojane materijalima koji proizvode određenu boju ili više boja. Nijansa i intenzitet samih boja ovisi o kemijskome sastavu stijenki keramike na koju se boja nanosi, o količini materijala upotrijebljenoga za bojanje, o vrsti i sastavu smjese te o temperaturi i atmosferi pečenja. Pigmenti (tvari kojima se boji) mogu biti organski ili anorganski, iako organski pigmenti najčešće oksidiraju i nestaju pri pečenju. Kao pigmenti koriste se prirodne rude, oksidi metala i umjetno napravljene mješavine (tablica 1) (Rice 1987: 148–149).

Najčešće se kao pigmenti koriste željezni oksidi. Pri pečenju mijenjaju prirodnu boju gline, a ako se dobro ne usitne, stvaraju tamne mrlje na keramici. Prema istraživanjima gline koje sadrže željezne okside (od 13 do 15%) peku se na temperaturi od 850 do 950 °C. Pri oksidaciji se od željeznoga oksida dobiva crvena boja, a pri redukciji crna boja. Gline u kojima željezo nije potpuno oksidiralo proizvode sivu boju (Betancourt & Swann 1989: 177–182). Keramika koja sadrži željezo tamni s porastom temperature iznad 1000 °C i u oksidacijskim uvjetima (Bimson 1979: 5).

Krajnja boja ovisi o kemijskome stanju željeza: oksidirano željezo Fe_2O_3 (hematit) proizvodi crvenu ili crvenkastosmeđu boju, dok se željezni sulfidi, karbonati, silikati i magnetit (Fe_3O_4) javljaju rjeđe i proizvode sivu, plavkastu, zelenkastu ili sivosmeđu boju. Boja ovisi i o količini željeznoga oksida u smjesi: 1% željeznoga oksida stvara žućkastu boju, 1,5–3% svijetlo smeđu ili narančastu, 3,5% ili više crvenu boju. Puna se boja javlja s porastom temperature na oko 900–950 °C (Rice 1987: 335–336).

Za proizvodnju keramike s bijelim premazom koriste se gline bogate kalcijem (Ca). Pigment kojim se postiže bijela boja mješavina je silikata kalcija te feldspata i kvarca. Nijanse bijeloga premaza nastaju zbog varijacija atmosfere u pećima tijekom pečenja (Grimanis *et al.* 1989: 169–175; Betancourt & Swann 1989: 177–182).

Ugljik (C) koji se javlja u raznim oblicima, od drvenoga ugljena u obliku praška do ekstrakata biljaka, može proizvesti samo crnu ili sivu boju i uvijek se nanosi nakon pečenja (Rice 1987: 148–149).

Boju proizvodi i vapno u određenim količinama. Promjene se javljaju pri visokim temperaturama na oko 800 °C i više. Kad se kalcij-karbonat (CaCO_3) raspadne i prijeđe u kalcijev oksid (CaO), može reagirati s glinom, pri čemu nastaje kalcijev silikat blijedožute ili bijele boje. Na temperaturi iznad 1000 °C vapno reagira sa željezom, potiskuje crvenu boju i prelazi u žutu ili maslinastozelenu boju.

they are applied, the quantity of material used for colouring, the type and composition of the compound and the firing temperature and atmosphere. Pigments (substances used to apply colour) may be organic or inorganic, although organic pigments most often oxidise and dissipate during firing. Ores, metal oxides, and artificial made mixtures (Table 1) are used as pigments (Rice 1987: 148–149).

Iron oxides are most often used as pigments. During firing they alter the natural colour of the clay, and if they are not ground well they create dark spots on the ceramic. Based on research, clays containing iron oxide (13–15%) are fired at temperatures of 850 to 950°C. During oxidation the iron oxide turns red, and black during reduction. Clays in which the iron does not entirely oxidise produce a grey colour (Betancourt & Swann 1989: 177–182). Ceramic containing iron becomes dark as the temperature rises above 1000°C under oxidising conditions (Bimson 1979: 5).

The ultimate colour depends on the chemical condition of the iron: ferric oxide, Fe_2O_3 (haematite) produces a red or reddish brown colour, while iron sulphides, carbonates, silicates and magnetite (Fe_3O_4) appear rarely and generate grey, bluish, greenish or grey-brown colours. The colour depends on the quantity of iron oxide in the clay mass: 1% ferric oxide creates a yellow colour, 1.5–3% light brown or orange, 3.5% or more red. The full colour appears with increasing temperatures at around 900–950°C (Rice 1987: 335–336).

Clays rich in calcium (Ca) are used to produce ceramic with white coating. The pigment used to attain the white colour is a mixture of calcium silicates and feldspar and quartz. Nuances in the white coating appear due to variations in the atmosphere in kilns during firing (Grimanis *et al.* 1989: 169–175; Betancourt & Swann 1989: 177–182).

Carbon (C), which appears in different forms, from powdered charcoal to plant extracts, may generate only black or grey colours and is always applied after firing (Rice 1987: 148–149).

In certain quantities, lime also produces colour. Changes appear at high temperatures of approximately 800°C and over. When calcium carbonate (CaCO_3) decomposes and becomes calcium oxide (CaO), it can react with the clay, and a white-yellow or white calcium silicate emerges. At temperatures higher than 1000°C, lime reacts with iron, displacing the red and turning into a yellow or olive-green.

Manganese (Mn) appears as red-brown lumps in clays found next to marshes. Manganese is added to the clay mass as powder and it produces a black colour.

U glinama koje se nalaze kraj močvara javlja se mangan (Mn) u obliku crvenosmeđih grumena. U glinenu smjesu mangan se dodaje kao prah i predmetu daje crnu boju.

Razni sulfidni i karbonatni minerali proizvode boje koje su nestabilne na temperaturama tijekom pečenja, ali se koriste za slikanje nakon pečenja. Tamno ružičastocrvena boja može se postići cinoberom (HgS) ili hematitom (Fe_2O_3) (Rice 1987: 336–337).

Osim glinenih premaza za postizanje kolorističkih efekata koriste se i glazure. Osim estetske uloge imaju i onu funkcionalnu. Glazurne smjese nanose se na pečenu površinu predmeta. Za izradu glazure koriste se minerali s niskom temperaturom topljenja kao što su olovo (Pb), bakar (Cu), alkalni metali⁶ itd. Pri izlaganju temperaturi mineral se u glazurnoj smjesi topi i pretvara u staklenu masu. Temperatura topljenja glazura varira od 900 do 1450 °C. Posude s glazurama ne propuštaju vodu, otporne su na kiseline i lakše se čiste.

Glazure se sastoje od:

1. kristalnih modifikacija silicijeva dioksida (SiO_2 – kremen, glinica, kvarc) koji se pri zagrijavanju zastakli;
2. aluminosilikata (soda, potaša, aluminijev oksid, pepeo biljaka, drveta, trava, lišća itd.) koji snižavaju temperaturu topljenja kristalnih modifikacija silicijeva dioksida (SiO_2) (inače se tope na temperaturi iznad 1700 °C) i time osiguravaju prijanjanje stakla u tekućem stanju za površinu predmeta;
3. metalnoga oksida koji daje boju glazuri (tablica 2) (Rice 1987: 150–151).

U olovne,⁷ bakrene ili alkalne glazure mogu se dodavati i drugi oksidi metala koji mijenjaju boju glazure. U olovnoj glazuri željezo stvara tople boje: svijetlo smeđu, žutosmeđu, boju jantara i crvenkastosmeđu boju. U alkalnim glazurama željezo daje hladne tonove u istome spektru boja. Krom (Cr) u glazurama s malo olova i bez cinka proizvodi zelenu boju, a s cinkom smeđu boju. U glazurama s olovom i s malo aluminija pri niskim temperaturama pečenja krom stvara narančastu ili crvenu boju, a na visokim temperaturama smeđu ili zelenu. Ako glina sadrži sodu, krom daje žutu boju. Mangan u alkalnim glazurama stvara plavoružičastu boju, a u olovnim glazurama svijetlo ružičastu (Rice 1987: 337–339).

Different sulphides and carbonate minerals generate colours that are unstable at high temperatures during firing, but they are used for decoration after firing. A dark pink-red can be obtained using cinnabar (HgS) or haematite (Fe_2O_3) (Rice 1987: 336–337).

In addition to clay slips, glazes are also used to achieve colourist effects. They have a functional as well as aesthetic role. Glaze mixtures are applied to the fired surface of an item. Minerals with low melting temperatures such as lead (Pb), copper (Cu), alkaline metals,⁶ etc. are used to make glazes. When exposed to high temperatures, the mineral in this glaze mixture melts and becomes a glassy mass. The melting point of the glaze varies from 900 to 1450°C. Glazed vessels are watertight, resistant to acid and easier to clean.

Glazes consist of:

1. crystal modifications of silicon dioxide (SiO_2 – flint, hydrated alumina, quartz) which vitrify when heated;
2. aluminosilicates (soda, potash, aluminium oxide, ash of burned plants, wood, grass, leaves, etc.) which lower the melting point of crystal modifications of silicon dioxide (SiO_2) (it otherwise melts at temperatures higher than 1700°C) and thereby ensures adhesion of the glass on the surface of the item in liquid form;
3. metal oxides which give colour to the glaze (Table 2) (Rice 1987: 150–151).

In lead,⁷ copper or alkaline glazes, other metal oxides can be added which change their colour. Iron creates warm colours in lead glazes: light brown, yellow-brown, amber and reddish brown. Iron produces cooler tones in the same spectrum of colours in alkaline glazes. Chromium (Cr) in glazes with trace amounts of lead and no zinc creates a green colour, and brown when there is zinc. In glazes with lead and a small amount of aluminium, chromium creates an orange or red colour when fired at low temperatures, and brown or green at high temperatures. If the clay contains soda, the chromium produces a yellow colour. Manganese in alkaline glazes creates a blue-pink colour, and light pink in lead glazes (Rice 1987: 337–339).

The glaze and structure of the item itself must be compatible due to potential contraction or expansion.

⁶ Alkalna glazura pečena je na relativno niskim temperaturama s visokom koncentracijom alkalnih metala u sastavu (naročito Na, K, Li). Važan sastojak često joj je pepeo drveta (Rice 1987: 471–485).

⁷ Olovne glazure, napravljene od mješavine olovnoga oksida i kvarca, samljevenih i pečenih na temperaturi od 800 do 1000 °C, otrovne su u dodiru s kiselinama iz hrane i tekućinama (Rice 1987: 100–101; Rye 1988: 44–47).

⁶ An alkaline glaze fired at relatively low temperatures with a high concentration of alkaline metals in composition (especially Na, K, Li). Charcoal is often a vital ingredient (Rice 1987: 471–485).

⁷ Lead glazes, made of blends of lead oxide and quartz, powdered and fired at temperatures of 800 to 1,000°C, become toxic when they come into contact with the acids in foods and liquids (Rice 1987: 100–101; Rye 1988: 44–47).

Razvoj boja glazura pri pečenju		
Oksidi	oksidacija	redukcija
Željezo (hematit)	žuta, smeđa, zelena s bakrom	siva, plava, zelena
Bakar	zelena, plava, plavozelena	crvena do ružičasta
Kobalt (od 0.25%)	plava	plava
Mangan (2–6%)	ružičasta, crna u kombinaciji sa željezom	smeđa

Development of glaze colours during firing		
Oxides	oxidation	reduction
Iron (haematite)	yellow, brown, green – with copper	grey, blue, green
Copper	green, blue, blue-green	red to pink
Cobalt (from 0.25%)	blue	blue
Manganese (2–6%)	pink, black in combination with iron	brown

Tablica 2. Razvoj boja glazura pri pečenju (Rice 1987: 337).

Table 2. Development of glaze colours during firing (Rice 1987: 337).

Glazura i struktura samoga predmeta moraju biti usklađene zbog mogućega stiskanja ili širenja u peći ili pri samoj uporabi predmeta. Rastopljene se glazure kemijski i mehanički sjedine sa stijenkama posuda stvarajući na površini čvršći ili mekši, tanji ili deblji sloj staklaste mase. U kemijskome smislu glazure su staklo.

Glazure se dijele na *prozirne* i *neprozirne*, a potonje na *bezbojne* i *obojene*. Boja glazure pri pečenju ovisi o vrsti i količini oksida upotrijebljenoga za bojenje, kemijskome sastavu stijenke keramike na koju se nanosi glazura, vrsti i sastavu glazure, temperaturi pečenja i atmosferi u peći. Zasićivanjem glazurne smjese oksidom metala (koji je upotrijebljen da bi se dobila određena boja) nastupa kristalizacija, to jest na površinu glazure izlučuje se kristal toga metala. Izlučivanjem kristala na površinu postiže se vrlo lijep dekor (Verigo 1960: 85–99; Horvat 1999: 25–28).

Predmeti se nakon pečenja mogu bojiti i zatim prelići glazurom. Takva boja zaštićena je od mehaničkih, kemijskih i drugih učinaka. U tom se postupku koriste boje otporne na djelovanje vrućih glazura i visokih temperatura pečenja te neosjetljive na redukcijske plinove u peći. Boje mogu biti *podglazurne* i *nadglazurne*. U podglazurne boje spadaju prirodne boje ili boje napravljene od oksida metala razmućenih u vodi uz dodatak bijele gline. Samljeveni materijal za bojenje, zajedno s dodacima, peče se na

in the kiln or during actual use of the item. Melted glazes chemically and mechanically bond with the walls of the vessel, creating a firmer or softer, thinner or thicker vitreous layer on the surface. In chemical terms, the glaze is then glass.

Glazes are classified as *transparent* and *opaque*, and that latter as *colourless* and *coloured*. The colour of the glaze at firing depends on the type and quantity of oxides used for colouring, the chemical composition of the surface of the ceramic to which the glaze is applied, the type and composition of the glaze, the firing temperature and atmosphere in the kiln. Saturation of the glaze mixture with a metal oxide (which is used to obtain a certain colour) causes crystallisation, i.e. the surface of glaze discharges crystals of that metal. Very attractive decorations are achieved when crystals are discharged on the surface (Verigo 1960: 85–99; Horvat 1999: 25–28).

After firing, items can be painted and then covered with a coating. Such paint is protected from mechanical, chemical and other effects. The paint used in this procedure is resistant to the effects of hot glazes and high firing temperatures and impervious to reduction gases in the kiln. Paints may be *underglaze* and *overglaze*. Underglaze paints include natural paints or paints made of metal oxides stirred in water with white clay added. Powdered painting materials, together with additives, are fired at temperatures ranging from 900 to 1000°C, after which

temperaturi od 900 do 1000 °C, nakon čega se melje u prah spreman za uporabu. Nadglazurnim bojama ukrašava se već glaziran i pečen predmet. To su staklene prašine niske točke topljenja, obojene primjesom većega ili manjega postotka materijala za bojenje (Verigo 1960: 107; Horvat 1999: 42–43).

PROCES PEČENJA KERAMIKE

Varijacije u strukturi keramičkoga materijala javljaju se i zbog razlika u procesu pečenja koji podrazumijeva temperaturu i atmosferu na kojoj se predmet peče (Shepard 1985: 6–48; Horvat 1999: 15–16). Prvi je i najjednostavniji način pečenje na otvorenome. Pomak u tehnologiji predstavlja zatvaranje prostora za pečenje, a golem je napredak postignut izumom keramičkih peći i odvajanjem keramičkih predmeta od vatrišta (Šimić-Kanaet 1990: 151–177). Otada se tehničko usavršavanje u keramičkoj proizvodnji svodi uglavnom na poboljšanje kvalitete glinene mase i glazure. Pečenje keramike kemijski je proces sagorijevanja glinenih minerala i ostalih organskih tvari grijanjem. Iz gline se prije pečenja mora isušiti mehanički vezana voda jer će čitav proces pečenja izdržati samo dobro osušena keramika. Proces sušenja ovisi o sastavu glinene mase, obliku predmeta i debljini stijenki. Keramički predmeti suše se postupno. Posude se prvo suše iznutra, a površina mora ostati vlažna sve dok se sva voda iz unutarnjih pora ne ispari jer zbog neravnomjernoga isušivanja mogu nastati pukotine. Predmeti se suše obično u prostorijama kroz koje dovoljno cirkulira zrak, najbolje u proljeće, ljeto ili ranu jesen. Brzina sušenja ovisi o prirodi gline i mineralima u njoj (Rye 1988: 23–24).

Nakon sušenja slijedi pečenje, zadnja faza u proizvodnji keramike. Svaka glina ima svoju temperaturu pečenja, što ovisi o njezinu mineralnome sastavu. Keramika se peče postupno i temperatura se povisuje u pravilnim razmacima, 40 °C – 80 °C – 120 °C (Hodges 1962: 58–69).

Fizičke i kemijske promjene, koje nastaju pri pečenju, ovise o trima čimbenicima:

1. o vremenu pečenja;
2. o temperaturi pečenja – kemijske reakcije počinju na točno određenim temperaturama; ako se promijeni ili povisi zadana temperatura, dolazi do deformacije predmeta ili čak do njegova raspadanja;
3. o atmosferi tijekom gorenja i hlađenja – atmosfera ovisi o količini zraka pri pečenju, potrebna za sagorijevanje dovoljne količine goriva; pečenje s nesmetanim protokom zraka i u prisutnosti kisika, koji se lako veže s elementima na površini ili u unutrašnjosti glinenih predmeta, odvija se pri oksidacijskoj

it is ground to powder and ready for use. Overglaze paints are used to decorate already glazed and fired items. These are glass powders with low melting points, dyed additives with lower or higher percentages of painting materials (Verigo 1960: 107; Horvat 1999: 42–43).

THE CERAMIC FIRING PROCESS

Variations in the structure of ceramic materials also appear due to differences in the firing process, which means the temperature and atmosphere at which the item is fired (Shepard 1985: 6–48; Horvat 1999: 15–16). The first and simplest method is firing in open air. Enclosure of the firing space signified a technological step forward, while the invention of the ceramic kiln and the separation of the ceramic item from the flame constituted immense progress (Šimić-Kanaet 1990: 151–177). Henceforth, the process of technical perfection in ceramic production was limited mainly to improvements in the quality of the clay mass and glaze. Firing ceramic is a chemical process involving the combustion of clay minerals and other organic substances by heating. The mechanically bonded water must be dried out of the clay prior to firing, because only well-dried ceramic will withstand the entire firing process. The drying process depends on the composition of the clay mass, the shape of the item and the thickness of its walls. Ceramic items dry gradually. Vessels first dry on the inside, while the surface must remain moist until all of the water from the internal pores evaporates, since uneven drying may lead to cracking. The items are normally dried in rooms with sufficient air circulation, best in the spring, summer or early autumn. The speed of drying depends on the nature of the clay and the minerals it contains (Rye 1988: 23–24).

Drying is followed by firing, the last phase in ceramic production. Each clay has its own firing temperature, which depends on its mineral composition. Ceramic is fired gradually and the temperature is increased at regular intervals, 40°C – 80°C – 120°C (Hodges 1962: 58–69).

Physical and chemical changes which occur during firing depend on three factors:

1. the duration of firing;
2. the firing temperature – chemical reactions begin at precisely specified temperatures; if the given temperature changes or increases, deformations or even shattering occur;
3. the atmosphere during heating and cooling – the atmosphere depends on the quantity of air needed

atmosfera; atmosferu pečenja pri kojoj nema kisika zovemo *redukcijska atmosfera* (Horvat 1999: 50–52). Promjene koje nastaju pri pečenju (na otvorenome ognjištu ili u zatvorenoj peći) mogu se pratiti u nekoliko faza.

A. ISPARAVANJE

Isparavanje se odvija na temperaturi do 120 °C. U toj se fazi iz gline u obliku vodene pare izlučuje voda. Predmet ostaje isti ili se tek neznatno počinje smanjivati.

Daljnijm praćenjem procesa pečenja utvrđeno je kako na temperaturi od 200 °C dolazi do raspadanja organskih tvari biljnoga porijekla koje se nalaze u glini.

B. TERMIČKO RASPADANJE GLINENIH MINERALA I SINTERIRANJE

Termičko raspadanje glinenih minerala i sinteriranje odvijaju se na temperaturi od 430 °C do 850 °C. Za neglaziranu keramiku to je glavna faza pečenja. Pri procjeni približne temperature pečenja keramike koriste nam primjese u glini koje, na točno određenim temperaturama, mijenjaju svoja primarna svojstva (npr. kremen (SiO_2) na 573 °C, kalcit (CaCO_3) na 740–800 °C, hematit (Fe_2O_3) i glineni minerali na 585 °C, montmorilonit na 678 °C). Sve vrste organskoga materijala, primarno prisutnih u glini ili umjetno dodanih glinenoj smjesi, počinju se raspadati, to jest oksidirati na temperaturi od 500 do 700 °C. Organske tvari izlaze iz unutrašnjosti na površinu stijenci gdje se oslobađaju u obliku ugljik-dioksida (CO_2). Pečenjem keramike na temperaturi do oko 900 °C u oksidacijskim uvjetima izgara sav ugljik osim grafita koji podnosi temperaturu do 1200 °C. Oksidacija ugljika brža je ako je keramika jako porozna, odnosno sporija što je poroznost predmeta manja.

Sinteriranje je faza pečenja u kojoj se pri povišenim temperaturama čestice u glini počinju mijenjati, taliti i međusobno spajati. Rezultat pečenja pri tako visokoj temperaturi jest kemijska reakcija sirovina, to jest stvaranje novih spojeva. Temperatura mora prijeći granicu na kojoj počinje proces sinteriranja, a mora proći i dovoljno vremena da se proces sinteriranja na dosegnutoj temperaturi završi. U protivnome može doći do ponovnoga spajanja s vodikom i uspostave prvotnoga stanja. Konačni rezultat sinteriranja je tvrđa, gušća i manje propusna stijenska, stabilna pri kemijskim i fizičkim promjenama.

Sve proizvode nastale na temperaturi između 430 i 850 °C možemo proglasiti keramičkim proizvodom. To je nepovratni proces prelaska glinene smjese u

when firing to combust sufficient quantities of fuel; firing with an unimpeded airflow and in the presence of oxygen, which easily bonds with elements on the surface or interior of the clay item, proceeds during oxidation in the atmosphere; a firing atmosphere without oxygen is called a *reduction atmosphere* (Horvat 1999: 50–52).

Changes which occur during firing (on open hearths or in closed kilns) may be followed over several phases.

A. EVAPORATION

Evaporation proceeds at temperatures up to 120 °C. In this phase, water in the form of water vapour is secreted from the clay. The item remains the same or its size only negligibly decreases.

Based on further monitoring of the firing process, it has been ascertained that at temperatures of 200 °C and over organic substances of plant origin found in the clay decompose.

B. THERMAL DECOMPOSITION OF CLAY MINERALS AND SINTERING

Thermal decomposition of clay minerals and sintering proceed at temperatures of 430 °C to 850 °C. This is the principal firing phase for unglazed ceramic. When estimating the approximate firing temperature, additives in clay are useful which, at specific temperatures, alter their primary properties (e.g. flint (SiO_2) at 573 °C, calcite (CaCO_3) at 740–800 °C, haematite (Fe_2O_3) and clay minerals at 585 °C, montmorillonite at 678 °C). All types of organic substances, initially present in the clay or artificially added to the clay mass, begin to decompose, that is, they oxidise at temperatures of 500 to 700 °C. Organic substances move from the interior to the surface of the walls where they are released as carbon dioxide (CO_2). Firing ceramic at temperatures up to approximately 900 °C under oxidation conditions burns out all carbon except graphite, which withstands temperatures up to 1200 °C. Oxidation of carbon is faster if the ceramic is very porous, and slower when porosity is lower.

Sintering is the firing phase when the particles in the clay begin to change, fuse and mutually coalesce at high temperatures. The result of firing at such high temperatures is a chemical reaction of the raw materials, i.e. the creation of new compounds. The temperature must pass the threshold at which sintering begins, and sufficient time must pass for sintering to finish at the proper temperature. Other-

keramiku (Weiß 1984: 55–57; Rice 1987: 93–96; Rye 1988: 25; Horvat 1999: 46, 50–52).

C. VITRIFIKACIJA

Vitrifikacija se odvija na temperaturi višoj od 900 ili 950 °C, pri čemu se stvara staklena struktura kao rezultat kontinuiranoga zagrijavanja i produženja tekuće faze sinteriranja. Specifična mješavina minerala u glini uvjetuje početak taljenja odnosno vitrifikacije. Vitrifikacija počinje kada se silikatni minerali i kisik, u unutrašnjosti stijenci glinenoga predmeta, dovoljno zagriju i počnu topiti u tekuću smjesu. Nakon konačne vitrifikacije stijenske su manje porozne i tvrde. Vitrifikacija se najprije prepoznaje po pojavi glatkih izoliranih dijelova prekrivenih staklenim nitima; zatim se staklene niti šire i postupno srastaju u jednoličnu glatku površinu. S porastom temperature pore se u keramici povećavaju. Taj stadij prethodi termičkoj deformaciji keramike na temperaturi od oko 1050 °C do 1100 °C pri redukcijске procesi ili na oko 1150 °C u oksidacijskoj atmosferi. Istraživanja su pokazala da se prema kompoziciji i strukturi vitrifikacije razvijene tijekom pečenja mogu razlikovati dvije grupe glina: vapnenaste gline i gline koje ne sadrže vapnenac. Kod glina koje su vapnenaste vitrifikacija počinje na temperaturama većim od 800 °C i stupanj vitrifikacije ostaje nepromijenjen pri rastu temperature od 850 °C do 1050 °C. Kod glina koje nisu vapnenaste stupanj vitrifikacije raste s porastom temperature (Maniatis & Tite 1981: 59–76; Rice 1987: 93–96). Sinteriranje i vitrifikacija počinju ranije u fine nego u grube keramike.

D. HLAĐENJE I PRAŽNENJE PEĆI

Proces je pečenja gotov kad se prestane dodavati novo gorivo ili kad gorivo izgori. Predmeti se hlade *oksidacijski* (uklanjaju se pepeo i žar s posuda) ili *redukcijски* (onemogućen je ulazak zraka i predmeti se prekrivaju pepelom), ako se želi postići da površina predmeta bude crna. Predmeti se uklanjaju iz peći tek kad temperatura padne ispod 40 °C (Horvat 1999: 50–52).

ZAKLJUČAK

Razlike koje se javljaju između gotovih keramičkih predmeta posljedica su razlika u strukturi keramičkoga materijala. Te varijacije javljaju se zbog kemijskoga sastava gline, primjesa koje mijenjaju svojstva gline pripremljene za oblikovanje, kao i razlika u procesu pečenja koji uključuje vrijeme pečenja,

wise renewed bonding with hydrogen may occur, re-establishing the initial condition. The final result of sintering is a harder, denser and less permeable ceramic material, stable during chemical and physical changes.

All products emerging at temperatures between 430 and 850°C can be called ceramics. This is the irreversible process of clay becoming ceramic (Weiß 1984: 55–57; Rice 1987: 93–96; Rye 1988: 25; Horvat 1999: 46, 50–52).

C. VITRIFICATION

Vitrification proceeds at temperatures higher than 900 or 950°C, when a glassy structure is created as a result of continued heating and extension of the current sintering phase. Specific blends of minerals in the clay cause the initiation of fusing or vitrification. Vitrification begins when silicate minerals and oxygen inside the walls of the clay item become sufficiently heated and begin to melt into the liquid mass. After final vitrification the walls are less porous and hard. Vitrification is first recognised by the appearance of smooth isolated parts covered with glass fibres; the glass fibres then expand and gradually grow into a uniform, smooth surface. As the temperature rises, the pores on the ceramic grow. This stage is preceded by thermal deformation of the ceramic at temperatures of approximately 1050°C to 1100°C during the reduction process or at approximately 1150°C in the oxidation atmosphere. Research has shown that based on the vitrification composition and structure that develop during firing, two groups of clay can be distinguished: lime clays and clays not containing lime. In case of lime clay, vitrification begins at temperatures higher than 800°C and the degree of vitrification remains unchanged when temperatures increase from 850°C to 1050°C. In case of clay without lime, vitrification increases as the temperature increases (Maniatis & Tite 1981: 59–76; Rice 1987: 93–96). Sintering and vitrification begin earlier in fine than in coarse ceramic.

D. COOLING AND EMPTYING THE KILN

The firing process is done when new fuel is no longer added or the fuel burns out. Items are cooled *oxidatively* (the ash and coals are removed from the vessel) or *reductively* (the inflow of air is prevented and items are covered with ash), if a black colour for the item's surface is desired. Items are removed from the kiln only when the temperature drops below 40°C (Horvat 1999: 50–52).

temperaturu i atmosferu u peći. Glavni je zadatak u proizvodnji keramike da proizvod služi predviđenoj svrsi. Uspjeh ovisi o keramičaru i njegovoj sposobnosti da pripravi smjesu odgovarajućih svojstava kojima će postići željeni rezultat. Čistoća sirovina, sastav smjese, atmosfera i temperatura pečenja različiti su za razne produkte.

Za istraživanje strukture keramičkoga materijala koriste se različite metode. Njima se nastoji utvrditi sastav glinene smjese i postoci raznih primjesa te objasniti kemijski procesi koji nastaju prilikom pečenja. Rezultati mogu dati predodžbu o porijeklu sirovinskoga materijala korištenoga pri izradi toga predmeta, potvrditi pripadnost određenoj radionici itd.

Za proučavanje i korištenje metoda za utvrđivanje koncentracije elemenata i strukture materijala koristi se termin *fingerprinting of pottery* (Kilikoglu *et al.* 1988: 37–46; Momsen *et al.* 1988: 47–57).

CONCLUSION

The differences apparent between finished ceramic products are the result of differences in the structure of the ceramic materials. These variations appear due to the chemical composition of the clay, the additives therein which alter the properties of the moulded clay, and as differences in the firing process which include the firing duration, temperature and atmosphere in the kiln. The principal objective in ceramic production is for the product to serve its planned purpose. Success depends on the ceramicist and his/her skill in preparing clay with suitable properties that will achieve the desired end. The purity of the raw materials, the composition of the mixture and the firing atmosphere and temperature are different for different products.

Different methods are used to study the structure of ceramic materials. These constitute an attempt to ascertain the composition of the clay mass and the percentages of various additives and explain the chemical processes which occur during firing. The results may provide an insight into the origin of the raw material used to make the item, confirm whether it was made in a specific workshop, etc.

The study and use of methods to ascertain the concentration of elements and the structure of materials are referred to as *fingerprinting of pottery* (Kilikoglu *et al.* 1988: 37–46; Momsen *et al.* 1988: 47–57).

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