

ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

MATERIAL AND ENVIRONMENT PROTECTION



ČASOPIS: ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

Glavni urednik: Dr Darko Vuksanović,
Univerzitet Crne Gore, Metalurško-
tehnološki fakultet

Uređivački odbor:

Dr Petar Živković, Crna Gora
Dr Jagoda Radošević, Hrvatska
Dr Miomir Pavlović, Srbija
Dr Dani Vrhovšek, Slovenija
Dr Kiril Lisičkov, Makedonija
Dr Tarik Kupusović, Bosna i Hercegovina
Dr Refik Zejničević, Crna Gora
Dr Časlav Lačnjevac, Srbija
Dr Ilija Nasov, Makedonija
Dr Goran Vujić, Srbija
Dr Niko Samec, Slovenija
Dr Ivan Gržetić, Srbija
Dr Željko Jaćimović, Crna Gora
Dr Nada Blagojević, Crna Gora
Dr Aleksandar Joksimović, Crna Gora

Izdavački savjet:

Dr Jelena Pješčić – predsjednik
Dr Ivana Bošković
Mr Dragan Radonjić
Dr Filip Kokalj
Mr Igor Jovanović

Za izdavača:

Prof. dr Darko Vuksanović

Izdavač:

Crnogorsko društvo za koroziju, zaštitu
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*Panevropski univerzitet APEIRON Banja Luka, Pere Krece 13. Banja Luka,
Bosna i Hercegovina*

Izvod:

Svjetska zajednica svakim danom uspostavlja sve novije strategije upravljanja otpacima u smislu sveobuhvatne reciklaže sekundarnih sirovina i bezbjednog odlaganja onih materijala koje mi do daljeg nismo u mogućnosti da iskoristimo. Teškoće obezbeđenja sredstava za opremanje savremenih sanitarnih deponija komunalnog smeća ili za postrojenja visoke tehnologije u skladu sa Internacionalnim standardima kvaliteta životne sredine ne smiju biti razlog da nastavimo da se prema otpadu odnosimo kao prirodnoj kategoriji. Da bi se eliminisale štetnosti bio-gasa iz deponija komunalnog otpada, nameće se potreba izgradnje i ugradnje sistema uređaja za otpolinjavanje deponija.

Ključne riječi: deponija, otpolinjavanje, komunalni otpad.

1. Uvod

Raspoloživa tehnologija daje potpuno za pravo tvrdnji da mi nismo spremni da pojmom otpada i deponija zamjenimo pojmovima sekundarna sirovina, emergent i veoma rentabilnim postrojenjima za reciklažu iskorišćenih sirovina i dobara. Kod manjeg broja specifičnih otpadnih materija za koje, za sada, ne postoje racionalna ili moguća rješenja ponovnog korišćenja, da obezbjedimo izgradnju posebnih depoa za njihovo odlaganje do eventualnog iskorišćenja.

Realnost današnjice nas upućuje na primjenu četri osnovna programska područja djelovanja u oblasti tretmana onoga što mi danas uslovno nazivamo krutim komunalnim otpadom[1]:

1.Smanjenje ukupne količine otpada (preventiva), što se realno lako može već danas postići primjenom čistih tehnologija, proizvodnjom čistih proizvoda i čistim uslugama.

2.Ponovno korišćenje sekundarnih sirovina, što se mora postići optimizacijom

unapređenja organizacije privrednih subjekata u oblasti otkupa, sakupljanja, prerade i prometa otpadaka neorganskog porijekla, kao i afirmacijom prerade otpadaka organskog porijekla, a sve pod uslovima bezbjednim i korisnim po životnu sredinu.

3.Unapređenje konačnog tretmana otpadaka, što se u našim uslovima postiže primjenom već postojeće zakonske regulative u oblasti urbanizma i zaštite životne sredine.

4.Formiranje i ospozobljavanje stručnih komunalnih službi za tretman svih vrsta otpadaka i istraživanje procesa iskorišćavanja otpada. Iskonsko pravilo prvobitnih ljudskih zajednica je bilo da svi oblici otpada imaju svoju upotrebnu vrijednost, a da to isto pravilo danas koriste zemlje sa razvijenom tehničkom, tehnološkom i ekonomskom kulturom.

Naš izlazak, opstanak i poslovni uspjeh na svjetskom tržištu limitiran je pored ostalog

i rezultatima svakog privrednog subjekta pojedinačno, ali i zajednice u cjelini po pitanju uspješnosti u upravljanju i zbrinjavanju svih vrsta otpadaka.

Našu donedavnu realnost najčešće su činila „smetljija“ koja smo pokušali nazvati „gradski deponijama“, jer su, a i danas, na njima završavala svoj put svi i sve sekundarne sirovine, bez obzira da li potiču iz naselja, fabrike, klanice, bolnice ili iz parkova.

2. Struktura otpada

Tabela 1. Struktura otpada

Vrste otpada	Zemlje razvijenih ekonomija(%)	Otpad USA (%)	Naši gradovi Banja Luka(%)
metali	6.0	7.0	2.1
staklo	8	6	4.5
plastika	8	8	5.1
papir	36	41	21.4
Organski otpad	24	25	53.4
Ostali otpad	18	13	11.5
Komunalni otpad	100	100	100

Sekundarne sirovine neorganskog porijekla, u otpadu zemalja sa razvijenom ekonomijom učestvuju 40% ukupne težine, u zemljama SAD sa 34%, dok u strukturi otpada grada Banja Luka one učestvuju sa 23.2%. Banja Luka ima relativno dobro razvijeno prethodno razdvajanje i sakupljanje sekundarnih sirovina.

Postavlja se zahtjev za boljim uvidom u proizvodnju otpada i za mehanizmima kojima bi se smanjilo, a zatim povratilo i recikliralo što je moguće više otpada na ekonomski isplativ način. Preostali otpad mora biti tretiran a zatim odložen na način koji minimizira posljedice po životnu sredinu. Vladajuće strukture moraju preuzeti jasniju odgovornost kroz

Utvrdjivanje strukture otpada je najznačajniji polazni element pri utvrđivanju načina upravljanja otpadom[2]. Struktura deponovanog smeća prema podacima komunalnih preduzeća BiH može nam dati samo okvirnu kvantifikaciju ali još uvijek sasvim dovoljnu za naše opredjeljenje o preduzimanju nužnih preventivnih mjera sanacije postojećih deponija (tabela 1.).

obezbeđenje politike, zakonodavstva, standarda, smjernica, određivanje naknada za usluge potrošačima, taxi ili podsticajnih mjera industriji za unapređenje upravljanja otpadom.

Činjenica da najveći dio otpadaka na našim deponijama čine otpaci organskog porijekla ukazuje na potrebu hitne optimizacije konačnog tretmana komunalnog otpada, kao i produkata koji nastaju razgradnjom biomasa odloženih u tijelu deponije.

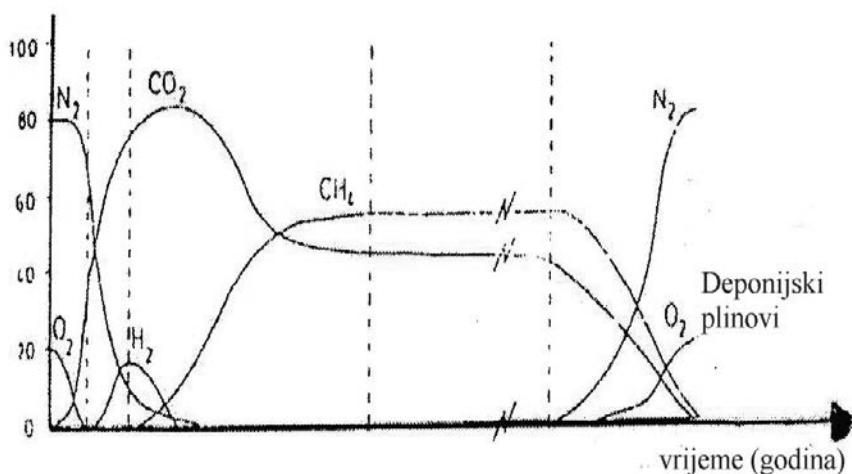
13. Nastanak deponijskog plina

Otpadne materije organskog porijekla u tijelu deponije podliježu složenom procesu razgradnje i procesu metanskog vrenja.

Nastajanje biogasa počinje po dovoženju i kompaktovanju otpada još uvijek u aerobnim uslovima u prisustvu vazduha koji se u pokrivenim i zbijenim slojevima relativno brzo iskoristi. Dalje nastajanje deponijskog plina procesima vrenja u

anaerobnim uslovima može se podjeliti u tri faze (slika 1.):

- kiselo vrenje sa emisijom CO_2 i H_2 , ali bez metana,
- nestabilno metansko vrenje u kome se učešće emisija ugljendioksida, azota i vodonika stabilizuje ili gubi, dok se emisija metana konsoliduje u količinama od 50-60 zapreminskih procenata biogasa,
- stabilizacija metanskog vrenja u anaerobnim uslovima.



Slika 1. Nastanak deponijskih plinova anaerobnom razgradnjom kućnog otpada na odlagalištu

Pored metana i ugljendioksida deponijski gas sadrži čitav niz materija u tragovima (dosad ih je istraženo stotinjak), od kojih je dosta otrovnih i kancerogenih (dioksini, furani, vinilhlorid, dihlormetan, toluol,

fenol i dr.). Uz deponijskih gas nastaje i prašina, koja može sadržavati otrovne teške metale i patogene klice (tabela 2.).

Tabela 2. Sastav deponijskih gasova (prosječna koncentracija)

SASTAV	KONCENTRACIJA (%)
Metan (CH ₄)	38-58
Ugljen dioksid (CO ₂)	30-48
Kiseonik (O ₂)	1-2
Azot (N ₂)	2-10
Vodonik (H ₂)	0-1
Ne-metanski ugljikovodici	<1
Isparljivi organski sastojci	=1
U TRAGOVIMA	(mg/m ³)
Sumporovodonik (H ₂ S)	0-150
Mirisi	10-1000
Organska jedinjenja hlora	0-800
Amonijak	0-100
Vinil hlorid i mnogi drugi	0-15 Od ppm do ppb nivoa

Zbog svih tih štetnih uticaja na zdravlje i okolinu započelo se prije nekoliko desetina godina u razvijenom svijetu sa kontrolisanim otplinjavanjem i spaljivanjem sakupljenog deponijskog gasa na bakljama. Sledeći logički korak bio je da se iskoristi energija deponijskog gasa, prvo u SAD sedamdesetih godina, a zatim i u razvijenim zemljama Evrope i ostatka svijeta[6].

Kod uredne ugradnje i zbijanja otpada, gas se može ne samo bolje nego i znatno ranije koristiti. U Njemačkoj se pokazalo, da se na mnogim deponijama poštovanjem specificiranih propisa za ugradnju, moglo eksploatirati već poslije pola godine iskoristive količine plina.

Ukupno trajanje stvaranja gase u deponijama iznosi prema teoretskim proračunima cca 100 godina. Međutim, ekonomsko korišćenje moguće je samo cca 30 godina.

Slijedeći parametri su od važnosti za kvalitet i kvantitet deponijskog gasa[1]:

- sadržaj vlage mora biti veći od 30%, jer je za bakterijsku razgradnju potrebna voda,

kao i kod svih bioloških procesa. Ispod 30% sadržaja vlage otpad se ne razgrađuje nego se mumificira. Zavisno od vrste otpada i položaja deponija može biti korisno kružno vođenje procjednih voda. Sadržaj vlage veći od 65% nije povoljan, jer se kod te sadržine izlučuje voda (prekoračenje kapaciteta polja).

- stepen zbijenosti otpada je važan, kako bi se efektivno sprječio ulazak kisika u otpadno tijelo. Kod visoke zbijenosti poboljšava se dostupnost organskih otpada mikroorganizmima, tako da je tok razgradnje efikasniji.

- organski dio je odlučujući za kvalitet i kvantitet deponijskog gasa. Iz kg raspoloživog organskog ugljika teoretski nastaje 1,8 m³ bioplina. Po toni kućnog otpada s udjelom organskih materija od cca 40-50% nastaje cca 150 m³ deponijskog plina.

4. Otplinjavanje deponija

Da bi se eliminisale štetnosti biogasa iz deponija komunalnog otpada i

omogućila optimalna melioracija i rekultivacija deponija, odnosno obezbjedila zaštitu od mogućih eksplozija i zaštita životne sredine (zdravlje ljudi, zemljište, vazduh, voda), nameće se potreba izgradnje i ugradnje sistema i uređaja za otpolinjavanje deponija komunalnog otpada, i to po prioritetu:

-sanacija postojećih smetlišta i deponija i -izgradnja sanitarnih deponija sa sistemom za otpolinjavanje deponijskog gasa[3].

Dosadašnja iskustva i rezultati već izgrađenih sistema za otpolinjavanje deponija potvrđuju da se ovdje radi o profitabilnim investicijama kojima se istovremeno dosadašnja deponija kao izvor štetnosti pretvara u „resurs“ za proizvodnju energije. Eliminišu se opasnosti po bezbjednost i zdravlje ljudi, a na poljoprivrednim i urbanim površinama omogućuje proizvodnja i boravak u uslovima normalne životne sredine, sve po načelima održivog razvoja i ekološke uravnoteženosti.

Pri sanaciji postojećih deponija, zavisno od kvantitativnih i kvalitativnih činjenica, pristupa se prelaznom rješenju ukopavanjem mreže cjevovoda za otpolinjavanje na dubini polovine do trećine dubine tijela deponije koji se vezuje na centralnu pumpnu stanicu za isisavanje deponijskih plinova. Odavde se deponijski plin odvodi do gorionika ili do termoenergetskih postrojenja.

Pretpostavka da je lokacija gradske deponije utvrđena kao optimalno prostorno i urbanističko rješenje urbane cjeline, nameće obavezu da se utvrdi jedinstveno tehničko-tehnološko i prostorno rješenje koje će omogućiti direktnu funkcionalnu povezanost sistema u dijelu sanacije i dijelu dalje izgradnje i uređenja savremene deponije komunalnog otpada.

Sve dok se u uslovima opšteg ekonomskog ograničenja odlaganje otpada bude rješavalo na deponijama smeća kao najjeftinijoj opciji, bićemo prinuđeni da naša prostorna i tehničko-tehnološka rješenja planiramo i realizujemo tako da se

u potpunosti mora eliminisati bilo koji pojavn oblik štetnosti na relaciji deponija-životna sredina.

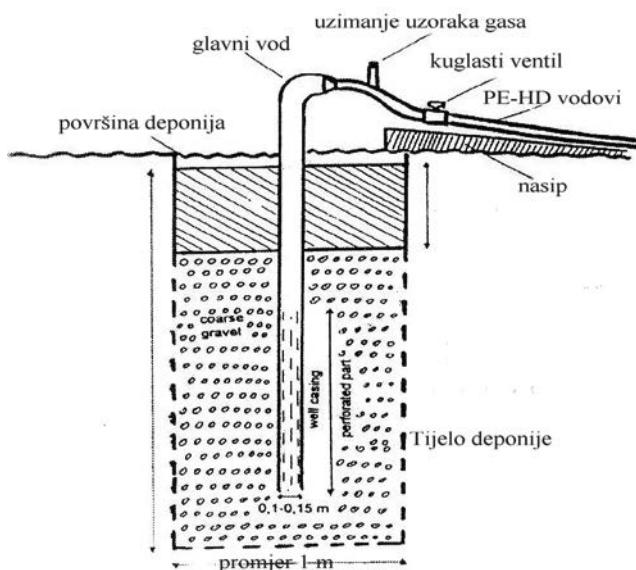
Osnovni principi savremeno koncipirane deponije komunalnog otpada, zavisno od konkretnih uslova sredine, ostvaruju se potpunom hidroizolacijom tijela deponije u cilju sprečavanja njenog vlaženja podzemnim, procjednim i površinskim vodama ili atmosferskim padavinama, optimalnim otpolinjavanjem deponijskih plinova i sprečavanjem emisija štetnih polutanata u vazduh i ostale resurse životne sredine.

Poslije aktivnog vijeka od oko 30 godina deponije se obično zatvaraju, ali se nastavlja generisanje deponijskih plinova i procjednih voda. Održavanje poslije zatvaranja je obavezno za sve lokacije gdje se komunalni otpad odlagao bez prethodne obrade. Brojni su primjeri gdje se deponije moraju vratiti u prvobitno stanje prije ili poslije zatvaranja, zbog negativnih uticaja koje imaju na životnu sredinu.

Vertikalni se bunari obično montiraju za sakupljanje deponijskih plinova na zatvorenim ili popunjениm dijelovima deponija[4]. Oni se mogu postaviti i na aktivnim deponijama, ali se u tom slučaju oplata bunara mora dograđivati u skladu sa dodatnim nasipanjem. Bunari su obično raspoređeni u trokutastoj rešetki tipskog među-razmaka od oko 60 m. Pravilo prakse je, minimalno jedan bunar na 4.000 m^2 deponije. Dubina bunara varira zavisno od uslova terena, ali je između 10 i 18 m uobičajeno. U SAD EPA je utvrdio projektni kriterij za bušenje bunara, preporučujući bušenje 75% dubine deponije ili bušenje do dubine nivoa vode, birajući pliću varijantu od ove dvije. Promjer bušenja je između 1 m i 0,6 m uključujući i oplatu bunara od 0,1 do 0,15 m. Oplata se sastoji od cijevi PE-HD koja se smješta u sredinu bušotine. Od jedne trećine do dvije trećine od dna oplata ima utore ili perforaciju, a bunar se puni krupnim šljunkom i brtvi na vrhu (npr. glinom ili muljem) protiv prodiranja vazduha. Na

vrhu oplate bunara pričvršćen je izlaz gasa koji je opremljen kuglastim ventilom radi kontrole protoka i otvorom za mjerjenje pritiska uzimanog uzorka gase. Izlaz je zaštićen kratkim betonskim prstenom i preko kuglastog ventila spojen na glavni

vod. Na slici 2. je shematski prikazan vertikalni bunar za otpolinjavanje starih deponija.



Slika 2. Vertikalni bunar za otpolinjavanje starih deponija

Za ekonomično korišćenje deponijskog plina trebaju biti ispunjeni slijedeći uslovi:

- minimum 1 milion metričkih tona komunalnog otpada,
- minimalna dubina otpada 10 m,
- lokacija nedavno zatvorena ili se još koristi za dovoz otpada,
- postoji površinski pokrov (bilo mulj ili zemlja)
- više od 100 mm kiše godišnje.

5. Korišćenje energije deponijskog plina

Zagrevna vrijednost deponijskog plina približno je upola manja nego kod prirodnog gasa (tabela 3.).

Tabela 3. Osnovna svojstva deponijskog plina

SVOJSTVA	DEPONIJSKI PLIN	PRIRODNI PLIN
Sadržaj metana (%vol.)	40-60	82-85.4
Zagrevna vrijednost (kWh/m ³)	4-6	9-11
Relativna gustoća	1.0	0.65
Stehijometrijska potreba vazduha za izgaranje (m ³ /m ³)	4.5-5.0	8.6-9.9
Metanski broj	140	87-70
Wobbe-broj (kWh/m ³)	5.57	12.4-15

U pogledu nekih svojstava izgaranja, deponijski plin je povoljniji od prirodnog plina, jer ima manje opterećenje gorionika (Wobbe-broj manji) i veću udarnu otpornost (metanski broj veći) od prirodnog plina. Deponijski plin se, kao i otpad, smatra obnovljivim energentom.

Tipična shema energetskog iskorišćenja deponijskog plina prikazana je na slici 3.

Deponijski plin nastaje kako na aktivnim tako i na napuštenim odlagalištima otpada još dugi niz godina poslije njihovog zatvaranja. Među izvedenim i planiranim postrojenjima energetskog korišćenja deponijskog plina dominiraju energane na odlagalištima sa proizvodnjom električne i toplotne energije u plinskim motorima (oko $\frac{3}{4}$ izvedenih objekata).

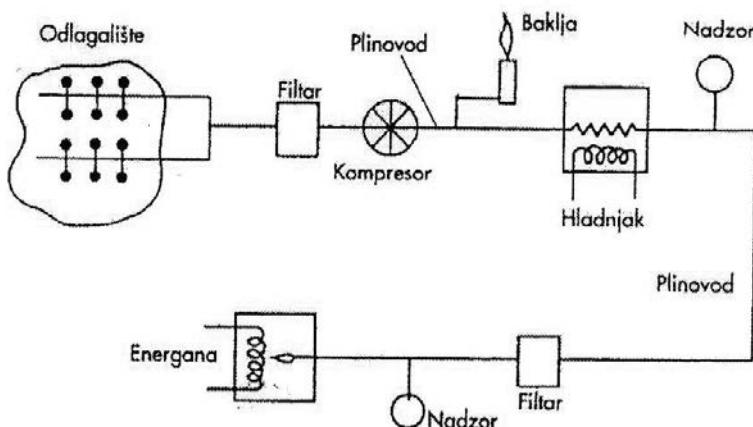
Obično se obrada plina sastoji od odvajanja kondenzata i isporučuje se plin kvaliteta od 30-50% CH₄. Lokalna upotreba plina može biti na čestici ili izvan čestice (u blizini) u industrijskom, stambenom ili komercijalnom objektu kojem je potrebna energija (npr. proizvodnja pare za grijage ili centralno grijanje). Druga je mogućnost generisanja električne energije, koja se

može koristiti lokalno ili isporučiti u elektroprivrednu mrežu. Za projekte korišćenja deponijskih plina za dobivanje energije, uobičajeni su motori s unutrašnjim sagorjevanjem (veličine 30 do 2000 kW) i ili plinske turbine (500 kW do 10 MW).

Ako nema lokalnog korisnika deponijskog plina dobra je opcija injektiranje u cjevovod. Rješenje zahtjeva komprimiranje plinova na pritisak u cjevovodu i obradu po standardima za cjevovode. To je kompleksniji i skuplji postupak. Dostupne tehnologije su: pritisna adsorpcija s ugljenim molekularnim sitom, aminijačno čišćenje i tehnika membrane.

U ovom slučaju četiri rezervna gorionika su montirana na distributivnoj stanici, i u njima deponijski plin izgara uvijek kada dođe do zastoja u sistemu korišćenja. Putem glavne sabirne cijevi ($d=0.28$ m) plin se vodi u kompresorsku stanicu, hlađi i komprimira na 2.5 bara. Konačno, putem transportnog cjevovoda plin se dostavlja toplotnoj stanici. Oko 950 m³/h deponijskog plina isporučuje se s minimalno 30% CH₄. Zavisno od CH₄ koncentracije (30-40%) energetska

vrijednost deponijskog plina varira od 15-20 MJ/m³. Sigurnosni sistem vodi računa o svim prekidima u mreži[5].



Slika 3. Energetsko iskorišćenje deponijskog plina

5.1 Proračun energetskog potencijala deponijskog plina

Cilj ove analize je odrediti iznos potencijalne količine električne energije dostupne iz komunalnog čvrstog otpada. Prema USEPA (United States Environment Protection Agency) efikasnost sistema za sakupljanje deponijskog plina iznosi 50-90%, a najčešće, uz primjenu dobre tehnologije 75-85%. Za ovu analizu usvojena je efikasnost sakupljanja od 80%. Toplotna moć deponijskog plina varira u zavisnosti od izvora u granicama 4,1-6,2 kWh/m³. Usvaja se 4,7 kWh/m³. Sa efikasnošću sakupljanja 80%, topotnom vrednosti od 4,7 kWh/m³ iz 1 kg komunalnog čvrstog otpada, trebalo bi se generisati 0,18 m³ deponijskog plina ($0,23 \text{ m}^3 \times 0,80 = 0,18 \text{ m}^3$) ili 0,85 kWh ($0,14 \text{ m}^3 \times 4,7 \text{ kWh/m}^3 = 0,85 \text{ kWh}$) tokom biološkog raspada komunalnog čvrstog otpada (20-25 godina). Vrijednost teoretskog maksimuma iznosila bi 0,3 m³ deponijskog plina/kg otpada ($0,38 \text{ m}^3 \times 0,80 = 0,3 \text{ m}^3$), ili 1,4 kWh ($0,3 \text{ m}^3 \times 4,7 \text{ kWh/m}^3 = 1,4 \text{ kWh}$), tokom biološkog raspada komunalnog čvrstog otpada.

5.1.1 Konverzija energije

Korišćenje deponijskog plina kao goriva za motore s unutrašnjim sagorevanjem je najrašireniji postupak njegove energetske valorizacije. Koristeći prethodne podatke, ovo se može prikazati na slijedeći način:

Ako usvojimo da je količina generisanja deponijskog plina tokom njegovog biološkog raspada u periodu od 20 godina, 0,23 m³/kg otpada, i računajući sa 80 % efikasnošću sistema za sakupljanje, dobijamo da 1 kg otpada generiše:
 $0,23 \text{ m}^3/\text{kg} \times 0,80 = 0,184 \text{ m}^3/\text{kg}$ tokom 20 godina

Iz ovoga slijedi da jedna tona otpada tokom 20 godina generiše:

$$0,184 \text{ m}^3/\text{kg} \times 1000 \text{ kg} = 184 \text{ m}^3 \text{ deponijskog plina.}$$

Ako računamo sa količinom od 81.000 tona koja predstavlja sadašnji trend odlaganja otpada na deponiji u Ramićima, da od toga 10% predstavlja količinu otpada koja neće generisati deponijski plin, dobijamo da bi tokom 20 godina odlaganja otpada imali potencijal generisanja deponijskog plina od:

$$184 \text{ m}^3 \times 81.000 \text{ t} \times 0,90 \times 20 \text{ god.} = 268.272.000 \text{ m}^3 \text{ u periodu od 20 godina}$$

Ako bi se kontrolom kvaliteta plina, motorima sa unutrašnjim sagorevanjem stavilo na rastpolaganje 80% ove količine dobijamo količinu od:

$$268.272.000 \text{ m}^3 \times 0,80 = 214.617.600 \text{ m}^3$$

što predstavlja ukupni energetski potencijal deponovanog otpada u periodu od 20 godina.

Količina potencijalnog generisanja deponijskog plina po 1h iznosi:

$$214.617.600 \text{ m}^3 / 20 \text{ god} / 365 \text{ dana} / 24\text{h} = \\ \mathbf{1.224 \text{ m}^3/\text{h}} \text{ deponijskog plina}$$

koji se može koristiti kao gorivo u motorima sa unutrašnjim sagorjevanjem. Računajući sa stepenom iskorišćenja

u periodu od 20 godina, čiji energetski potencijal, ako računamo sa toplotnom vrijednosti deponijskog plina $4,66 \text{ kWh/m}^3$, iznosi:

$$214.617.600 \text{ m}^3 \times 4,66 \text{ kWh/m}^3 = \\ \mathbf{1.000.118.016 kWh}$$

motora od 0,40, i toplotnom vrijednosti deponijskog plina od $4,66 \text{ kWh/m}^3$ dobijemo da potencijalna snaga bi trebala iznositi:

$$1.224 \text{ m}^3/\text{h} \times 0,40 \times 4,66 \text{ kWh/m}^3 = 2.281,5 \text{ kW} = 2,2 \text{ MW}$$

Zaključak

Upravljanje kvalitetom životne sredine i uspostavljanje ekološke ravnoteže naših potreba i mogućnosti okruženja, dovode nas do neminovnosti da se otpadne materije moraju koristiti ili kao sekundarne sirovine postupkom reciklaže ili kao energetski resurs postupkom potpunog intenzivnog otplinjavanja tijela deponije.

Ako u zemljama članicama Evropske unije mogu sa potpunom rentabilnošću da otplinjavaju svoje deponije, tada mi imamo još više razloga da iskoristimo naše deponije i da evidentnu štetnost po životnu sredinu iskoristimo za privredni i društveni razvoj.

Na primjeru regionalne deponije komunalnog otpada Ramići-Banja Luka, je pokazan energetski potencijal deponovanog otpada u periodu od 20 godina kao i količina potencijalnog generisanja deponijskog plina po 1h.

Uvezši u obzir da procenjena količina otpada koja je odložena na deponiji u Ramićima iznosi oko 1.800.000 tona, možemo zaključiti da su i trenutni uslovi za sakupljanje i iskorišćenje deponijskog plina realni, kao i da u budućnosti možemo očekivati i povećanje količina generisanja deponijskog plina uslijed povećanja količina otpada koje će se odlagati na deponiji u Ramićima.

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BIOGAS POTENTIAL OF MUNICIPAL WASTE OF CITY OF BANJA LUKA

Veljko Đukić

*Pan-European University APEIRON Banja Luka, Pere Krece 13. Banja Luka,
Bosnia and Herzegovina*

Abstract

The world community every day establishes newer waste management strategy in terms of a comprehensive recycling of secondary raw materials and safe disposal of those materials that we do not further able to use. The difficulties of providing funds for the equipment of modern sanitary landfills for municipal waste facilities or high technology in accordance with International environmental quality standards should not be a reason to continue to relate to waste as a natural category. In order to eliminate the dangers of bio-gas from municipal waste landfills, there is need for the construction and installation of equipment for landfill degasification.

Key words: *landfill, degasification, municipal waste.*

THERMAL AND ENVIRONMENTAL CHARACTERISTICS OF GLASS PRODUCED FROM METALLURGICAL WASTES

Ejup Ljatifi¹, Alexandra Kamusheva², Goran Načevski¹, Emilia Karamanova², Aleksandar Petrovski¹, Alexander Karamanov², Perica Paunović¹

¹ - Faculty of Technology and Metallurgy, University "Sts. Cyril and Methodius"

Ruger Bosković Str., 16, 1000 Skopje, R. Macedonia

² - Institute of Physical Chemistry, Bulgarian Academy of Sciences,
Acad.G.Bonchev Str., Bl.11, 1113 Sofia, Bulgaria

Abstract

The subject of this study is glass produced by mixed metallurgical waste from ferronickel production, aimed for further production of glass-ceramic. Characterization of waste materials includes determination of chemical and mineralogical composition and standard leaching test. The waste materials contain several heavy metals (Fe, Ni, Mn, Zn, Cr) which exceed the applied limits and can be potential hazard to the soils. On the other hand, the waste mixture contains sufficient amount of glass-forming component - SiO₂. The components in the waste mixture aimed for glass production were in the ratio as they are produced in the Fe-Ni smelter (fly ash:electro-furnace slag:converter slag = 1:10:1). Thermal characterization of the glass was performed by means of hot stage microscopy (HSM) and DTA analysis, where the temperatures of sintering, softening, smelting and crystallization were determined. The results highlight that fine-crystalline glass-ceramic with high crystallinity can be obtained. Standard leaching test has shown that the concentration of all heavy metals is below applied limits for 5 to 400 times. Thus, the produced glass is environmental safety product.

Keywords: fly ash, electric furnace slag, converter slag, glass, glass-ceramic

1. Introduction

Disposal or stabilization of waste materials from metallurgical industry such as slags, dust, hydrometallurgical by-products etc., is not an easy task because of the complex composition and high content of regulated heavy metals as well as different local circumstances. Often, recovery of some metal can not be economic efficient or the recovery procedure produce new waste. Disposal of waste containing heavy metals can be hazardous to environment. Vitrification of hazardous wastes, i.e. transformation of waste materials to glass can be considered as an environmentally compatible stabilization process. It is considered as an ultimate method for immobilization hazardous wastes, because during glass

melting, the harmful elements are chemically bonded in a durable amorphous network [1-3]. This significantly reduces their solubility and, in addition, drastically decreases waste in volume. On the other hand, depending on the composition, with or without any additives, the waste-based glass can be transformed to glass-ceramic with properties comparable or better than commercial ones. This is illustrated by numerous researches focused on using slags originated from iron and steel production for production of glass or glass-ceramic [4-10]. The research of Karamanov and co-workers was directed on production of glass and glass ceramic from by-products originated from zinc and copper hydrometallurgical production [11-15]. All

these studies highlight good chemical, physical and mechanical properties of the produced glass or glass-ceramic, close or even better than those produced from virgin raw materials. Besides technical and economic effects, this route of processing metallurgical waste materials was shown as environmental efficient. According to various standard leaching tests [16], the glass and glass-ceramic products based on

metallurgical waste, are environmental friendly materials.

The aim of this study is vitrification of solid waste from ferronickel smelting plant, such as dust, slag from electro-furnace and converter slag. Characterization of waste materials and produced glass is directed to estimate their possibility for further production of glass-ceramic as well as to determine their environmental impact.

2. Experimental

Dust (D), electro-furnace slag (EFS) and converter slag (CS) from ferronickel smelting plant in R. Macedonia, were used as a raw material for glass production. Their annual production is in ratio D:EFS:CS = 1:10:1. The content of different type of waste was in this ratio within the waste mixture aimed for vitrification.

Chemical composition of the waste materials was determined by X-ray fluorescence (XRF) spectrometer (Model XRF ARL 9900). Mineralogical analysis was carried out by X-ray diffraction method using Philips APD 15 diffractometer,

operating at CuK α -radiation. Diffraction data were collected at a constant rate of $0.02^{\circ}\cdot\text{s}^{-1}$ over an angle range of $2\theta = 5\text{--}90^{\circ}$.

To determine environmental impact of the waste materials, standard leaching test – TCLP (Toxicity Characteristic Leaching Procedure) was performed. Shown in Table 1 are the leaching test conditions. Concentrations of heavy metals after testing were measured by atomic absorption spectroscopy (AAS) using the instrumentation Perkin Elmer AA400.

Table 1. Leaching conditions according to TCLP test

Solvent	CH ₃ COOH
pH	5
Volume of the solution	2 L
Weight of solid phase	100 g
s:l ratio	1: 20
Intensity	30 rpm
Duration	24 h

To correct the content of MgO and Cr₂O₃ in the waste mixture (WM), standard glass (SG) powder was added in ratio WM:SG = 7:3. Waste materials and the standard glass were homogenized and melted in chamber furnace at 1450°C for 1 h.

During the heating reduction of dimensions and characteristic temperatures were

Thermal characteristics of the produced glass were studied by means of hot stage microscopy (HSM) and differential thermal analysis (DTA). A glass sample was observed in heating microscope MISURA HSML. The sample was heated from ambient to 1300°C with heating rate of $1^{\circ}\text{C}\cdot\text{min}^{-1}$.

recorded. DTA measurements were performed using a Perkin Elmer PYRIS

Diamond Thermogravimetric/Differential Thermal Analyzer. The studied material was heated in the temperature interval of $25^{\circ}\text{C} \div 1100^{\circ}\text{C}$ by heating rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ air atmosphere.

The glass sample was undergoing on standard TCLP leaching test. The test conditions are the same as in previous case shown in Table 1.

3. Results and discussion

Chemical composition of the waste materials is shown in Table 2. All waste materials have high amount of Fe, especially converter slag (CS). So, these wastes could be used for Fe extraction, but, there is not smelter for iron production in R, Macedonia. Only in the dust Ni content is appropriate to be returned in the Fe-Ni production process. Annual production of these waste materials is 102.000 t dust, 1.135.000 t slag from electro-furnace and 109.000 t converter slag. The ratio of their production is approximately D:EFS:CS = 1:10:1. On the other hand, the dust and slag from electro-furnace contain high enough

SiO_2 - glass forming component. Also, the waste mixture has appropriate content of SiO_2 (47.8%) for glass forming. But, MgO and Cr_2O_3 is high in the waste mixture (15.9 and 2.2 % respectively) and can cause spontaneous uncontrolled crystallization. Cr_2O_3 is not soluble in the glass, while in lower amount can improve the nucleation during transformation of glass to glass-ceramic. Thus, the composition of the waste mixture should be corrected in order to reduce the content of MgO and Cr_2O_3 . For this purpose standard glass (SG) was added in the waste mixture in ratio WM:SG = 7:3.

Table 2. Composition (wt%) of dust (D), slag from electro-furnace (EFS), converter slag (CS), waste mixture (WM) in ratio D:EFS:CS = 1:10:1, standard glass and overall glass mixture in ratio WM:SG = 7:3

Item	D	EFS	CS	WM	SG	GM
SiO_2	37.5	53	1.9	47.8	71.4	55
MgO	14.5	16.9	6.2	15.9	3.3	12.1
CaO	2.3	2.4	15.9	3.5	9.8	5.4
Al_2O_3	1.8	2	0.3	1.9	0.6	1.5
Cr_2O_3	1	2.5	0.7	2.2		1.5
CoO	0.1	0.1	0.1	0.1		0.1
NiO	2.7	0.1	0.45	0.3		0.2
Fe_2O_3	30	14	60	19		13.3
FeO		9	19	9		6.5
Na_2O					13.3	4
K_2O					1.3	0.4

The waste mixture as well as the overall glass mixture is iron-rich. It is similar to a typical natural petrurgical raw material - basalt rock [17,18], containing typically Fe rich phases in glass-ceramic, also typical for waste-derived glasses, have been shown to impart functional properties to the final products [7]. As magnetic, electrical and thermal properties of glass-ceramics can be altered by controlling the crystalline phase concentrations, crystallisation kinetic studies of iron rich silicate waste derived glass-ceramic are important for optimising functional properties [7, 12].

According to XRD analysis (Fig. 1), iron is present as hematite (Fe_2O_3 , i.e. Fe^{3+} form) and as non-stoichiometric mixed oxide with Cu, Zn and Cr ($\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_{1.1}\text{Fe}_{0.9}\text{O}_4$) in the dust. The similar appearance of iron is in slag of electro-furnace – non-stoichiometric mixed silicate (forsterite) and non-stoichiometric Fe^{3+} oxide – maghemite. Converter slag contains Fe^{3+} as hematite and calcium iron oxide (CaFe_2O_4), Fe^{2+} as wuestite and mixed Fe^{3+} and Fe^{2+} oxide – magnetite (Fe_3O_4). The glass forming component – SiO_2 is present as pure oxide quartz and silicates with other metals, mainly with Mg and Ca. According to the Fe content and appearance, it is

10–15 wt% iron oxides and it is characterized by high chemical durability and good resistance to abrasion and corrosion.

expected to produce glass similar to basalt based one [17].

The results of the TCLP test, carried out on the waste materials and produced glass are summarized in Table 3. There are several metals which exceed the applied limits and can be potential hazard to environment if the waste materials would be disposed at landfill. Ni, Mn, Zn, As and Cu are hazardous components in the dust, in the electric-furnace slag are Fe, Ni and Mn, while in converter slag are Fe, Ni and Cr. Concentration of Fe and Ni are to far from the applied limits.

One of possible and effective options to immobilize heavy metals is to capture them in glass matrix after vitrification of waste materials. So, next step in this research was vitrification of mixture of waste materials and standard glass. To ensure transformation of the mixture in liquid state, vitrification was performed at 1450°C for 1 hour. After cooling at ambient temperature, the produced glass was undergone to thermal investigations.

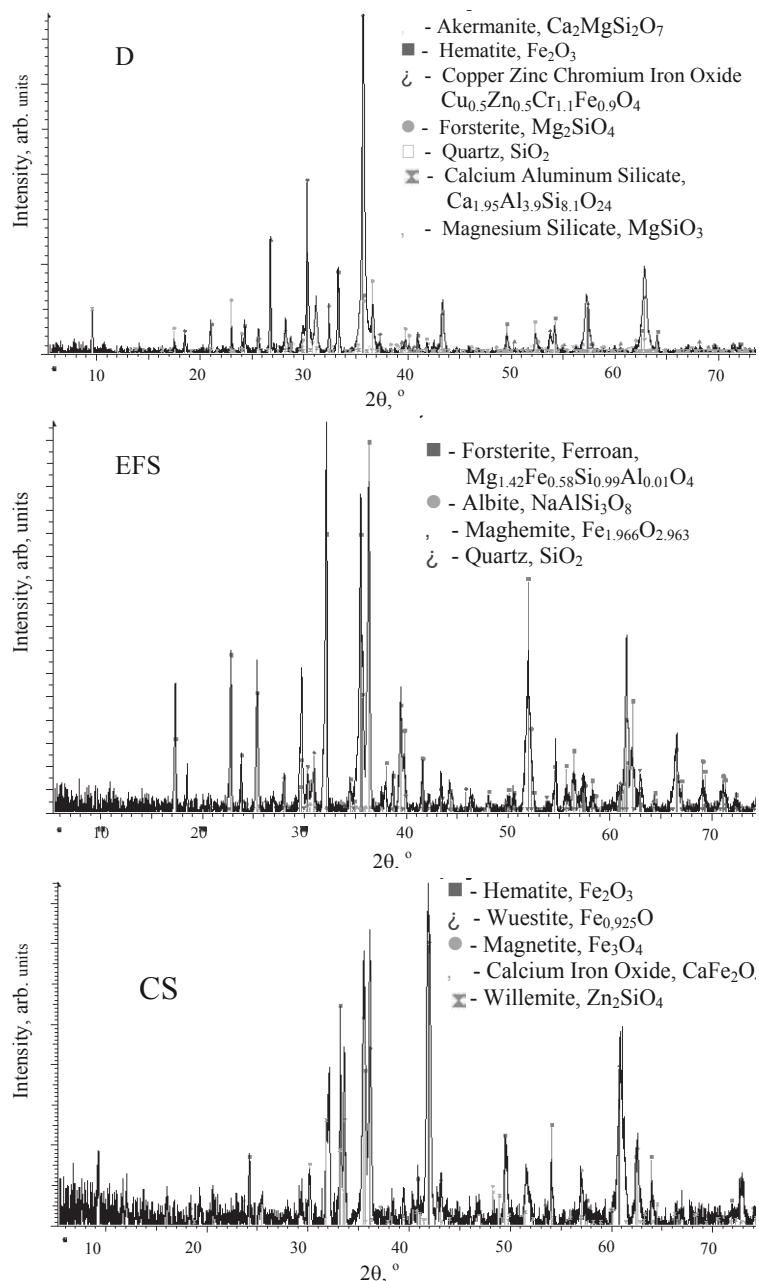


Figure 1. XRD spectra of the waste materials

Hot-stage microscopy is an analytical technique which combines the best properties of microscopy and thermal analysis to enable the characterization of the physical properties of materials as a function of temperature. During the measurements, video and pictures of the sample were recorded with registered reduction of dimensions. Also, a diagram temperature – change of dimensions (%) was constructed and determined temperatures of sintering, softening and

melting were determined (Fig. 2). Produced glass shows high stability of dimensions and shape during the heating. The sintering occurs at high temperature (1167°C) at very short interval and practically this material does not sinter. At sintering temperature reduction of dimension is very low. Lowering of dimensions to 78.25% of starting ones reaches at softening temperature at 1222°C , but the shape is still stable. Forming of half-sphere occurs at 1245°C and melting point is 1251°C .

This is relatively low melting point, which contributes to more economically efficient process of vitrification of waste based glass. The HSM results, obtained by pressed glass powders, highlight that the sintering method

is not appropriated for the investigated glass, because the traditional low-temperature densification is totally inhibited by intensive crystallization.

Table 3. Concentration of heavy metals in the solution after TCLP test

	D, mg·dm ⁻³	EFS, mg·dm ⁻³	CS, mg·dm ⁻³	Glass, mg·dm ⁻³	Applied limits, mg·dm ⁻³
Fe	1	202	1155	0.416	2
Ni	6,1	2.7	19.2	0.311	2
Co	0.4	0.14	1.1	< 0.005	2
Cd	< 0.005	< 0.005	< 0.005	< 0.005	0.02
Cu	0.15	0.093	0.07	0.011	0.1
Mn	4.7	14.6	1.5	< 0.005	2
Pb	0.026	0.031	0.086	0.017	0.2
Zn	3.6	0.29	0.42	< 0.005	2
Cr	0.22	1.1	2.9	< 0.005	2
Sb	0.020	0.038	0.023	0.023	
As	1.2	0.011	0.18	0.009	5

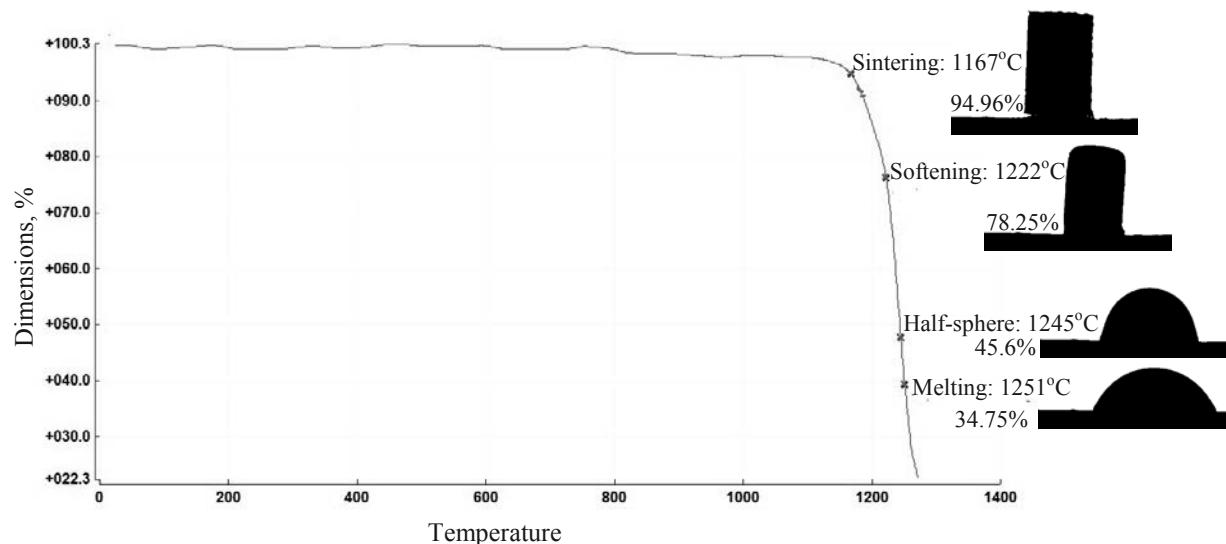


Figure 2. Change of dimensions as function of heating temperature registered by HSM

In order to determine how and at which temperature the studied glass crystallize, DTA analysis was performed at temperature region from ambient to 1100°C by heating rate of 20°C·min⁻¹. Crystallization of the waste based glass occurs at 800°C. The shape and the intensity of peak indicate intensive bulk crystallization. If we previously perform

nucleation of glass with retention of heating at 650°C for 1 hour, the temperature of crystallization shifts to lower temperature of 785°C, while the intensity of the bulk crystallization increases. This points out that the waste based glass is appropriate for production of glass-ceramic and can be performed by two-stage process: firstly heating at 650°C to perform nucleation and crystal growth at 785°C.

At the same time, the preliminary DTA and density results demonstrate that this composition have good trend for bulk

nucleation, giving possibility to obtain material with fine crystalline structure at low temperatures and short times.

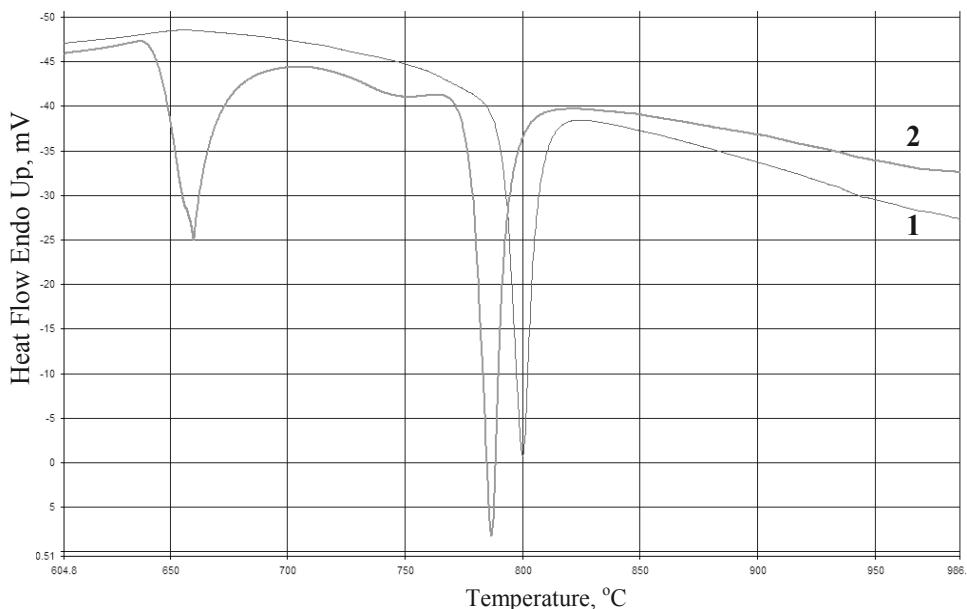


Figure 3. DTA curves of the studied waste based glass: non-nucleated (line 1) and nucleated at 650°C (line 2)

TCLP test of the produced glass was performed, in order to evaluate the environmental impact. The results of TCLP test are given in Table 3. The results show

the vitrification procedure is successful and that the obtained glass demonstrates high chemical durability, corresponding to an inert material.

Conclusion

According to the obtained results from this study, we can draw several conclusions: Waste materials from ferronickel production process contain components which are potential hazard to environment.

Waste materials contain glass-forming components enough, so they are appropriate for vitrification and further transformation of the produced glass to glass ceramic.

TCLP test of the produced waste based glass has shown that it is environmental friendly, i.e. the amount of all heavy metals in the leachate is far below the applied limits.

The produced waste based glass has shown very short interval of sintering at high temperature (1167°C) and low melting point, which point out on its economical efficient production at lower temperatures.

The produced glass showed intensive bulk crystallization at 800°C without previous nucleation. Nucleation at 650°C for 1 hour decreased the crystallization temperature to 785°C, as well as increased the intensity of the bulk crystallization. This offers possibility for efficient two-stage production of glass-ceramic from the studied glass: 1st stage of nucleation at 650°C and 2nd step crystallization at 785°C.

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DETERMINING GRAPHENE LAYERS NUMBER AND N-LAYER REGION COVERAGE BY XRD DATA DISTRIBUTION MODEL

Beti ANDONOVIC, Anita GROZDANOV, Aleksandar PETROVSKI, Perica PAUNOVIC,
Aleksandar DIMITROV

*Faculty of Technology and Metallurgy, SS Cyril and Methodius University, Skopje, Macedonia
beti@tmf.ukim.edu.mk*

Abstract

A model consisting of an equation which includes graphene thickness distribution is used to calculate theoretical 002 XRD peak intensities. An analysis was performed upon graphene samples produced by two different electrochemical procedures: electrolysis in aqueous electrolyte and electrolysis in molten salts, both using reverse change of the applied potential. The model applied to the corresponding 2θ interval enables obtaining theoretical curves that exhibit fitting with a sufficient accuracy to the XRD intensities curves of the studied graphene samples. The employed equation parameters make it possible to calculate the n-layer graphene regions coverage of the graphene samples, and the average value for number of graphene layers. Results of the analysis are in agreement with the calculated number of graphene layers from Raman spectra C-peak position values, and indicate that graphene samples are few-layered.

Key words: Graphene, electrochemical production, XRD analysis, layers.

1. Introduction

Graphene is 2D building unit of all wide-variety carbon allotropes, having unique and exotic properties largely due to its structure. Graphene can be produced by many ways such as mechanical exfoliation of graphite, chemical vapor deposition (CVD) of carbon bearing gases on the surface of copper films [3], cutting open nanotubes [4]. Electrochemical approach is a proven low-cost method for a high-yield production of graphene.

Depending on the production procedure, graphene can be produced as a mixture of

monolayers, bi-layers and multilayers (3–10 monolayers) in form of flakes or flat sheets [5].

Herein, an XRD pattern around a graphene 002 peak was used for layer number non-uniform distribution determination for graphene samples obtained by two different electrochemical procedures: electrolysis in aqueous electrolyte and electrolysis in molten salts, both using reverse potential.

2. Model that provides calculation of graphene thickness distribution by XRD data

The XRD pattern was analyzed by using the following Equation 1 that uses Laue functions which includes graphene thickness

distribution and certain parameters, hence XRD intensities of the curves were calculated thereof: [6]

$$|F|^2 \sim |f(\theta)|^2 \left| \sum_{j=0}^N \beta_j e^{ika_j i} \right|^2 \quad (1)$$

where F is a structure factor, N is the number of graphene layer, $|f(\theta)|$ is an atomic scattering factor which varies from 6.00 to 6.15 e/atom with incident radiation ranging from 2 to 433 KeV, $ka_j = (4\pi d_j \sin \theta) / \lambda$, where d_j is a lattice spacing between j th and $(j-1)$ th layer, θ is an angle between the incident ray and the scattering planes, λ is a

wavelength of X-ray, and β_j is an occupancy of j th graphene layer. The value of β_j is between 0 and 1. The employed equation parameters β_j make it possible to calculate the n-layer graphene regions coverage of the graphene samples produced by the two electrochemical procedures.

2.1. Graphene produced by electrolysis in molten salts and model (1)

Two graphene samples produced by electrolysis in molten salts are considered and

discussed herein: graphene sample 2G and graphene sample x.

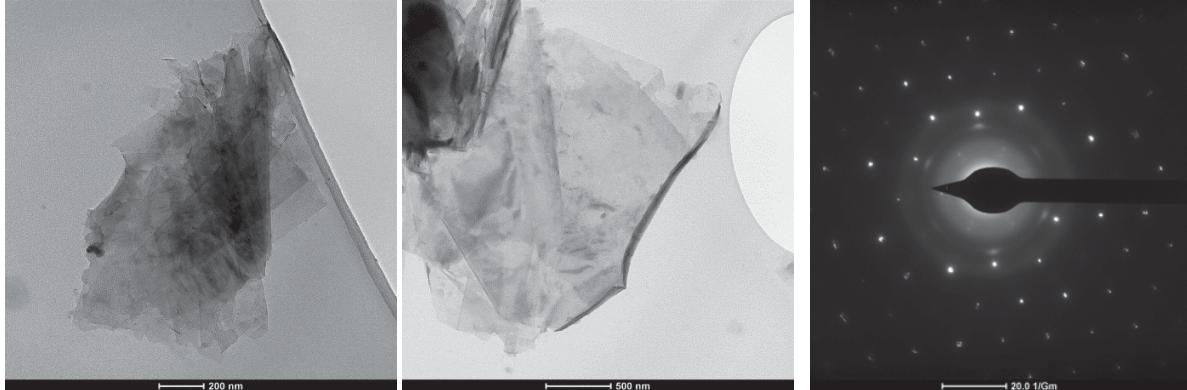


Figure 1. a) TEM images of 2G graphene sheets; b) Diffraction pattern of image

Using Eq. (1), XRD intensities of the curves in Fig. 2 are calculated as further discussed. The three red lines are calculated curves from

the Eq. 1 for $\beta_j \neq 1$, which suggests that the number of graphene layers has a distribution.

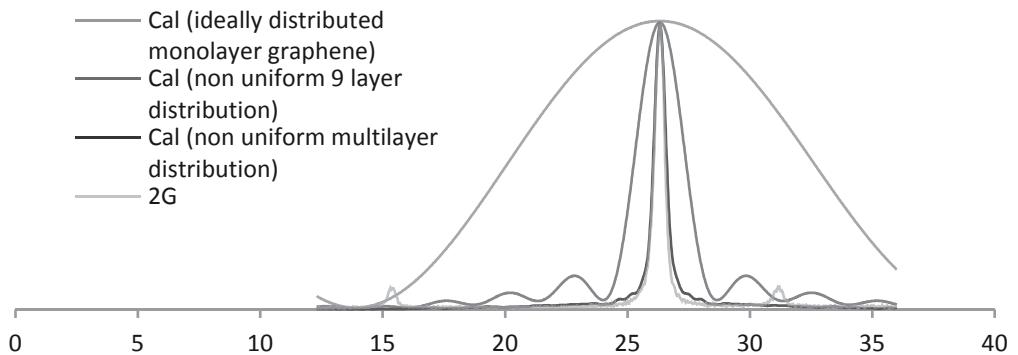


Figure 2. Non uniform multilayer distribution curve for Sample 2G calculated from Eq.(1)

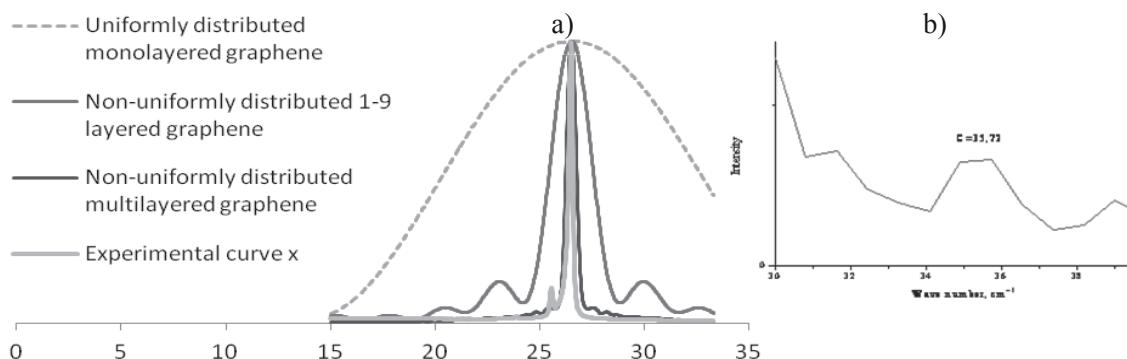
The broadest red dotted line in Fig. 2 is calculated curve for ideally distributed monolayer graphene, the light red line which is narrower than the monolayer graphene line, but broader than the green experimental curve, is calculated curve for a non uniform distribution of graphene layers number for a 9-layered graphene. The dark red line is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene, which exhibits a good fitting to the experimental curve, as it is symmetrical and the correlation coefficient is $\rho = 0.986$. According to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 1 a).

Apparently, the dominant structure is few-layered, and the average value for number of graphene 2G layers is calculated as $N_{GL}=2.87$ for the dominant structure and $N_{GL}=5.16$ for the overall structure.

In Fig.3 a), there are calculated theoretical curves from Eq. 1 presented in red, for graphene sample x, and the experimental curve x in green. In Fig 3 b), there is part of the Raman spectrum for sample x, showing off its C-peak. Its position $Pos(C)_N$ is directly connected to the graphene layers number N , and it varies with N as in the formula: [7]

$$Pos(C)_N = \sqrt{\frac{2\alpha}{\mu}} \sqrt{1 + \cos\left(\frac{\pi}{N}\right)}$$

where $\alpha = 12.8 \times 10^{18} \text{ Nm}^{-3}$ is the interlayer coupling, and $\mu = 7.6 \times 10^{-27} \text{ kg A}^{\circ -2}$ is the graphene mass per unit area.



*Figure 3. a) Non uniform multilayer distribution curve for Sample x calculated from Eq. I;
b) C-peak position in Raman spectrum for graphene sample x*

According to the analysis of the XRD 002 peak, the n layer region coverages are as in Table 1 b).

*Table 1. a) Coverages of n-layer 2G graphene regions
b) Coverages of n-layer x graphene regions*

a)	Monolayer region coverage	~ 35%	b)	Monolayer region coverage	~ 18.75%
	2-3 layers region coverage	~ 5-10%		2 layers region coverage	~ 21.25%
	5-6 layers region coverage	~ 5%		3 layers region coverage	~ 3.75%
	7-8 layers region coverage	~ 5%		4-6 layers region coverage	~ 2.5%
	9-10 layers region coverage	~ 5%		7-8 layers region coverage	~ 2.5%
	> 10 layers region coverage	< 20%		9-10 layers region coverage	~ 1.25%
				> 10 layers region coverage	< 25%

The average value for number of graphene x layers is calculated as $N_{GL}=2.4$ for the dominant structure and $N_{GL}=7.43$ for the overall structure.

According to the C-peak position, the number of graphene x layers for sample x is $N=2.54$.

2.2. Graphene produced by electrolysis in aqueous electrolyte and model (1)

Graphene samples 4 and 10 produced by electrolysis in aqueous solution, using reverse potential, are considered herein and analyzed.

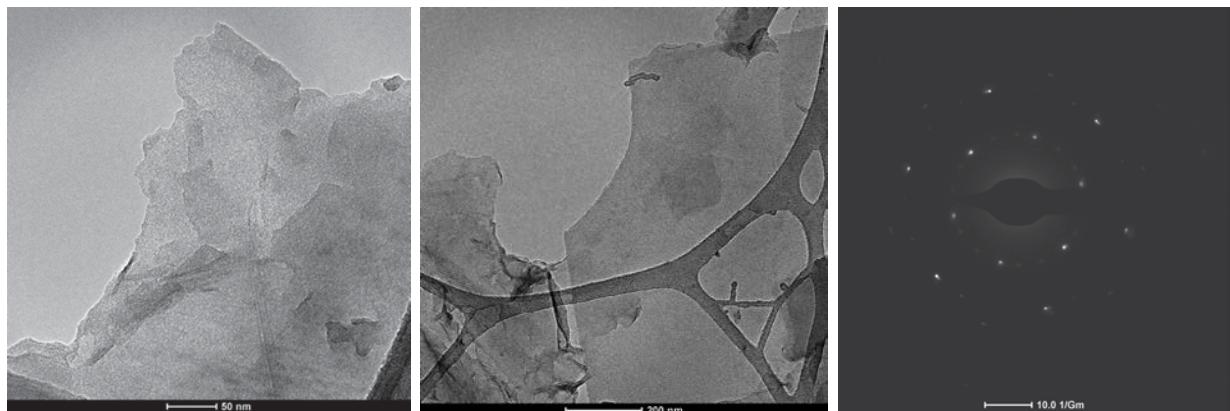


Figure 4. a) TEM images of Sample 4 graphene sheets; b) Diffraction pattern of image

The three blue lines in Fig. 5 are calculated curves from the Eq. 1 for $\beta_j \neq 1$, which suggests that the number of graphene layers has a distribution.

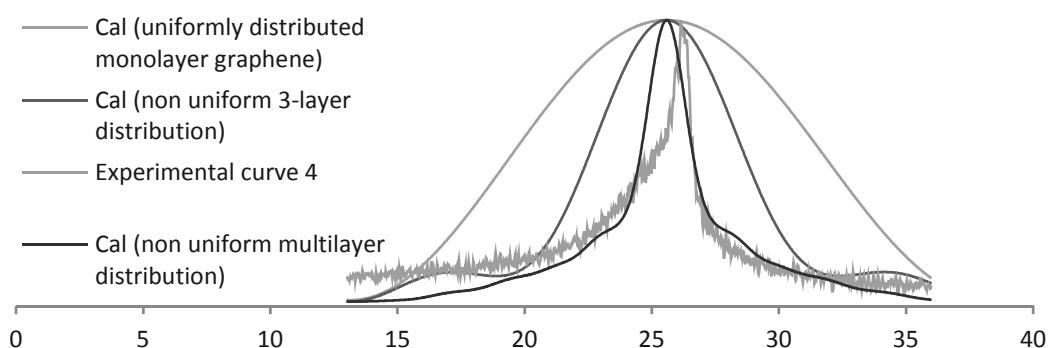


Figure 5. Non uniform multilayer distribution curve for Sample 4 calculated from Eq.1

The broadest blue dotted line in Fig. 5 is calculated curve for uniformly distributed monolayer graphene, the light blue line which is narrower than the monolayer graphene line, but broader than the green experimental curve 4, is calculated curve for a non uniform distribution of graphene layers number for a 3-layered graphene. The dark blue line is calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene. There is a noticeable discrepancy with the experimental curve due to its asymmetry. However, as the correlation coefficient is $\rho = 0.92$, it provides an additional insight into n-layer graphene regions share, and the results are in agreement with the results

obtained by other methods. According to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 2 a).

According to these calculations, the dominant structure is few-layered, and the average value for number of sample 4 graphene layers is calculated as $N_{GL}=2.57$ for the dominant graphene structure and $N_{GL}=4.25$ for the overall graphene structure.

In Fig. 6 the three blue lines are calculated curves from the Eq. 1 for $\beta_j \neq 1$, which again suggests that the number of graphene layers has a distribution.

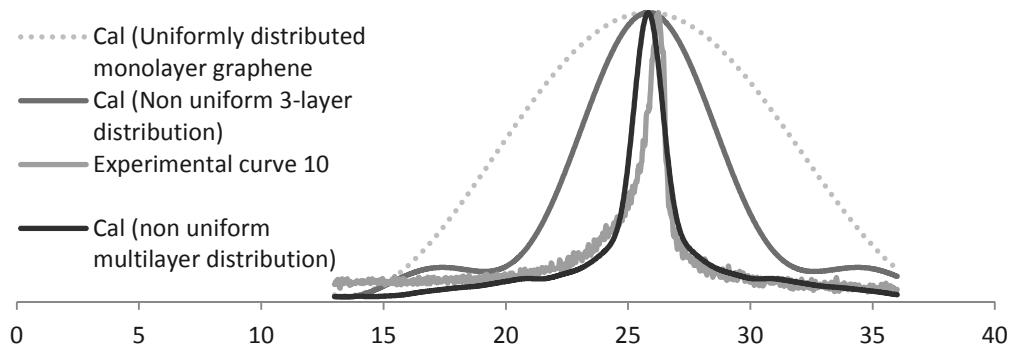


Figure 6. Non uniform multilayer distribution curve for Sample 4 calculated from Eq.1

The broadest blue dotted line is calculated curve for uniformly distributed monolayer graphene, the light blue line which is narrower than the monolayer graphene line, but broader than the green experimental curve 10, is calculated curve for a non uniform distribution of graphene layers number for a 3-layered graphene. The dark blue line is

calculated curve for a non uniform distribution of graphene layers number for a multi-layered graphene with a correlation coefficient $\rho = 0.93$, and according to its β_j parameters, the coverages of n-layer graphene regions are calculated as in Table 2 b).

Table 2. a) Coverages of n-layer graphene sample 4 regions
b) Coverages of n-layer graphene sample 10 regions

a)	Monolayer region coverage	$\sim 40\%$	b)	Monolayer region coverage	$\sim 30-35\%$
	2 layers region coverage	$\sim 10\%$		3-4 layers region coverage	$\sim 5-10\%$
	3-6 layers region coverage	$\sim 15\%$		5-6 layers region coverage	$\sim 5-10\%$
	7-10 layers region coverage	$\sim 5\%$		7-10 layers region coverage	$\sim 5-10\%$
	> 10 layers region coverage	$< 10\%$		> 10 layers region coverage	$< 10\%$

The dominant structure is few-layered, and the average value for number of sample 10 graphene layers is calculated as $N_{GL}=3.53$ for

the dominant graphene structure and $N_{GL}=5.6$ for the overall graphene structure.

3. Conclusions

There are several clear conclusions to be drawn from the preceding analysis. The model that is used provides an additional insight into graphene samples n-layer occupancies and therefore coverages with a sufficient accuracy. However, a limitation to this model that should not be disregarded is the fact that in general case graphene sheets which are subject of research may have layer structure that varies across the studied sample and hence an asymmetrical 002 XRD peak. Experimental 002 XRD peaks which are highly asymmetrical are inconvenient to be analyzed by this model, and therefore adequate alterations to the model should be considered and researched. The results relevant to graphene samples produced by electrolysis in aqueous electrolyte and by electrolysis in molten salts, both using reverse change of the applied potential, which were studied and analyzed herein using this model, are in accordance with other methods results, and have shown that these graphene samples are few-layered.

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DESIGN AND ANALYSIS OF THE PROCESS OF INCINERATION OF STABILIZED SLUDGE FROM COMBINED WASTEWATER SOURCES

Kiril Lisichkov^{1*}, Ljatifi Mahi¹, Gjorgji Zhezhov¹, Stefan Kuvendziev¹, Mirko Marinkovski¹, Zoran Bozhinovski²

¹ University "Ss. Cyril and Methodius" Skopje, Macedonia, Faculty of Technology and Metallurgy,
Ul. Rudež Bošković 16

² "Water Supply and Sewage", Public Enterprise, Skopje, Macedonia, Center for Sanitary Control

Abstract

The global industrial development requires an appropriate development of green processes with zero impact on the environment and full energy efficiency in order to provide sustainable development of our societies. Hence, a sustainable process design is a major challenge on each step of the process. To build a design of a wastewater treatment plant with zero impact on the environment, suitable solution needs to be employed for the stabilized sludge. This paper will make a review of the process simulations done to present the alternative solutions for stabilized sludge disposals, as the incineration and agriculture uses are. Process simulation will present a tool for designing and analyzing of the process models. Stabilized sludge composition depending, incineration will be chosen as a model for energy obtaining process, or stabilized sludge will be used for agriculture purposes. Stabilized sludge will be obtained from the WWTP "AD OHIS" in Skopje, which combine industrial and municipal wastewater treatment.

Key words: environmental process design, wastewater sludge treatment, SuperPro Designer, incineration

Introduction

During process development, process simulation software is used to perform material and energy balances, estimate the size of equipment, calculate demand for utilities as a function of time, asses the environmental impact, etc. With the further expansion of the public sewage system in city of Skopje and the expansion of the simulated process scheme that will follow

of advanced treatment, it is predicted that amount of sludge generated, electric power and energy consumption and the greenhouse gas emission levels will increase. To meet these challenges the new technologies must be developed and introduced as a program that is promoting emission reduction measures. up the simulated process scheme for remodeling of the wastewater treatment

* klisickov@yahoo.com; phone: +389 71 391 433; fax: +389 2 3065 389

plant "AD OHIS" in Skopje for treatment of wastewater from combined sources. Attention has been focused on the sewage sludge that has been treated by incineration until the present, and the process scheme

Materials and methods

The flow sheet is developed by putting together the required unit procedures, and joining them with material flow streams. This process starts with continuous effluent feed stream, which represent the activated sludge from the plant for secondary wastewater treatment "AD OHIS" in Skopje. This stream is characterized with sludge flow of $3.7 \text{ m}^3/\text{h}$, generated by $150 \text{ m}^3/\text{h}$ of treated wastewater. Sludge has content of 4% solids and 96% water. Detailed sludge non volatile content is showed below in Table 1, and Table 2 (1).

The first step in process scheme is stabilizing the activated sludge produced as by product from the "AD OHIS" Skopje wastewater treatment plant. Stabilizing process is starting with sludge dewatering in digester P- 11/ SLDR- 101 showed in Figure1, where 65% of the water is evaporated using air which can be pre heated using heat from the incinerator. Then, sludge is passing through the belt filter press P-13/ BF- 101 where solid concentration of the sludge is increasing from 35% to 80%. These two equipments are working continuously. Now stabilized sludge in this form is transferred using elevator P-10/ BE- 101 to the top of the

was designed to optimize the energy conversion and minimize the remained unused energy from the incineration process up to now to a usable energy.

incineration oven P-1/ INC- 101. On start up this equipment is using fuel to start the sludge incineration, and in our design case propane is used. Incineration is held at 950°C with 30% excess of oxygen and using propane as a start up fuel, Figure 2. After incineration flue gas is generated at temperature of 950°C containing 1% of ash particles. Gas cyclone P-12/ CY- 101 is the next procedure where set point of 90% of the ash particles will be settled down, and with the ash from the oven are discharged. Further, flue gas heat is exchanged with shell and tube heat exchangers P-2, 3/ HX- 101,102 (2, 3). Optimum heat exchanging will be further examined using process simulations. At the end of the process, flue gas is cleaned from the HCl and SO_2 , and the remaining ash particles as well using electrostatic precipitation and Na(OH)_2 absorption process (3-7).

The exit flue gas temperature is set up at 950°C , and excess oxygen at 30%. These incinerator parameters are important for calculation of the excess heat produced by amount of sludge incinerated. In the next figure is shown flue gas temperature versus excess heat dependence, obtained from several process simulations (2, 3)

Results and discussion

From the simulation report we have clear view of the results for the material balances for each material component in the system, total material balances, and material balances for each flow separately

and in total. Also heat exchangers were optimized, regarding the exchange area, amount of water for cooling and hot water exit heat shown in Table 3.

After the simulations were done, for the standard stabilized sludge feed obtained from the wastewater treatment plant at “AD OHIS” Skopje, process simulator was operated in calculated mode, and optimal size of heat exchangers was calculated, and the optimal amount of cold water as well , Table 3. Further, for constant heat exchanging area and constant size of equipment, optimal amount of cold water, optimal heat exchange area, and maximum stabilized sludge feed was achieved.

From the Figure 4, and Figure 5 showed below, for optimal heat exchange area for

serial connection of heat exchangers can be considered 121 m² and 3500 kg/h supply of cold water and for parallel connection of the heat exchangers optimal heat exchanging area can be considered 137 m² and cold water supply of 3700 kg/h. In this case exit temperature of the flue gas after the heat exchangers is 120 °C, comparing with the serial exchangers where exit temperature of gas is 170 °C. In the following Table 4 is described the material balances of the waste streams.

Conclusion

Process simulation software can play an important role during process development, and can significantly make the progress faster. Because of the nature of the combination of the process of incineration and not present of heavy metals or any other toxic components, there is no need of adding of additional filters with special characteristics for flue gas cleaning. From the simulations done we have obtained an optimal exchanging area for the cooling of the flue gas and obtaining a clean

energy with minimizing energy loses. At the end we have simulated one green energy process which can be further optimized for the future needs. Further the ash from the incineration can be used for regeneration of the metals contained. Optimum heat exchange area is obtained for the lower value at the lower amount of cold water that need to be used for cooling of the streams, and optimum value for the cold water is obtained at a value for amount that will exchange more heat.

Table 1. Sludge non- volatile content percent

Sludge non volatile content (%)					
Al	Ca	Fe	K	Mg	Na
0,15	27,5	2,4	0,02	0,27	0,08

Table 2. Sludge non- volatile content mass concentration

Sludge non volatile content (mg/kg)											
As	Ba	Cd	Cr	Cu	Li	Mn	Ni	P	Pb	V	Zn
<10	120	<1	32	103	1	90	22	775	57	7	232

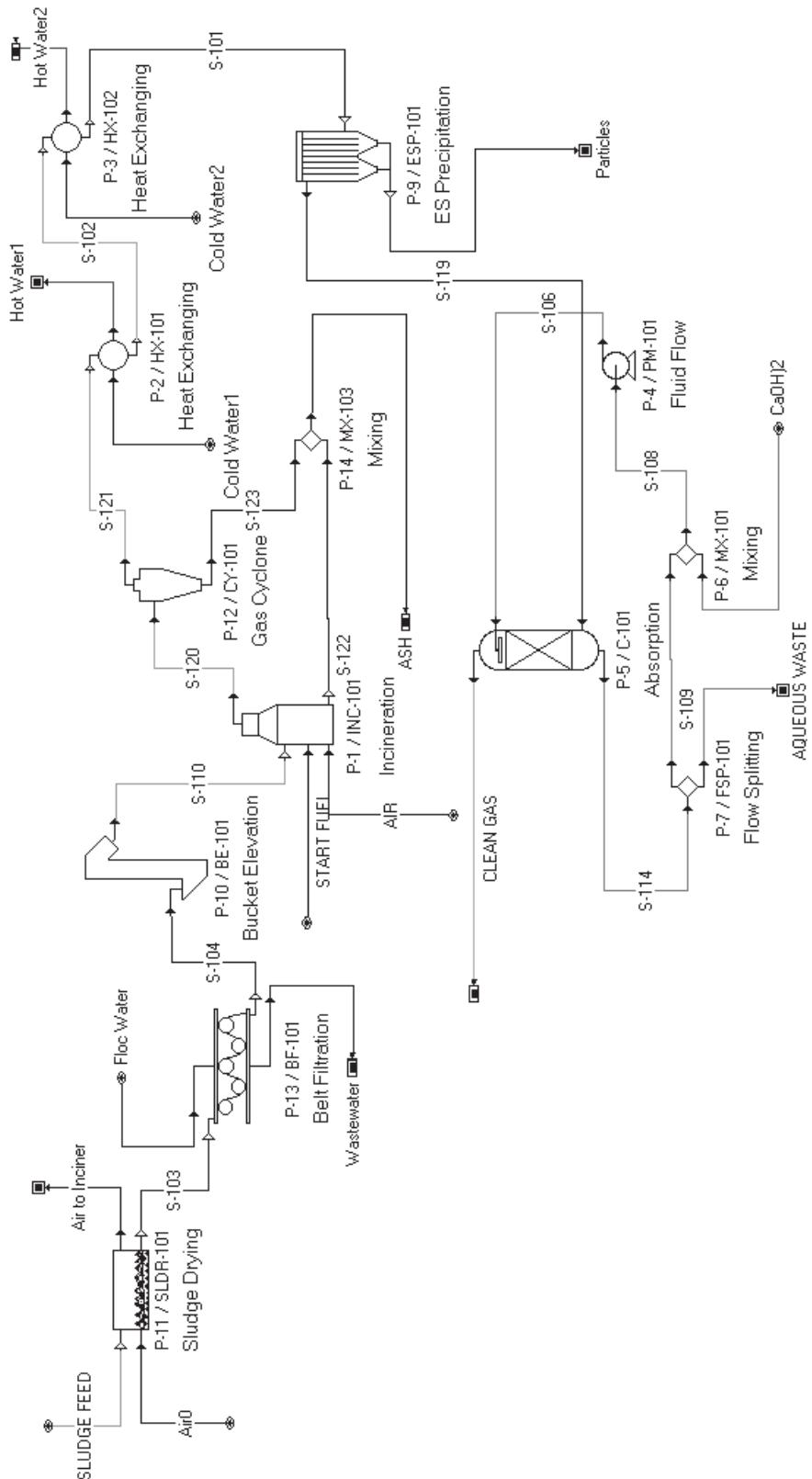


Figure 1. SuperPro Designer scheme of the sludge incineration process

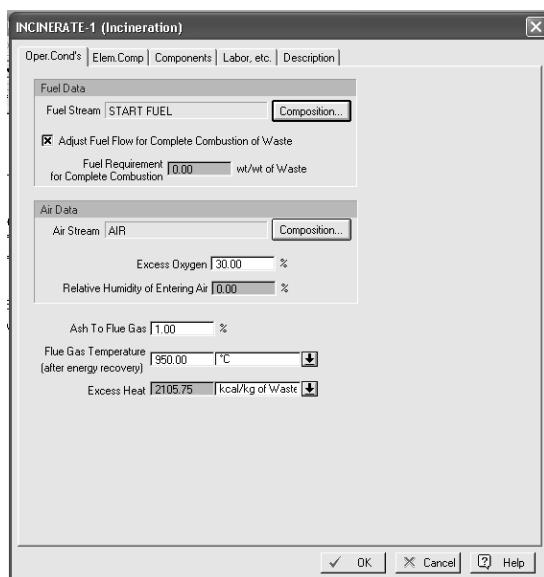


Figure 2. Incineration procedure simulation window with set up points

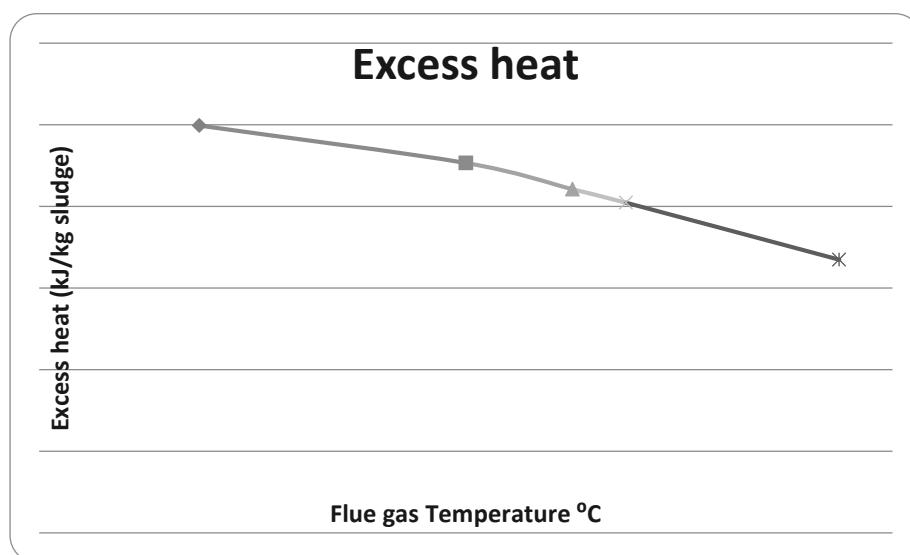


Figure 3. Excess heat dependence of exit flue gas

Table 3. Heat exchangers main parameters, simulated values

	Sludge flow 188 kg/h
Heat exchanging area	11,805 m ²
Quantity of cold water supplied; temperature	1 m ³ /h; 20°C
Quantity of heated water; temperature	1m ³ /h ; 182 °C
Utilization of flue gas heat	61%
Flue gas quantity; temperature	0,429 m ³ /h; 1000 °C
Heat transfer coefficient (specified for incineration flue gas)	100 Watt/m ² K

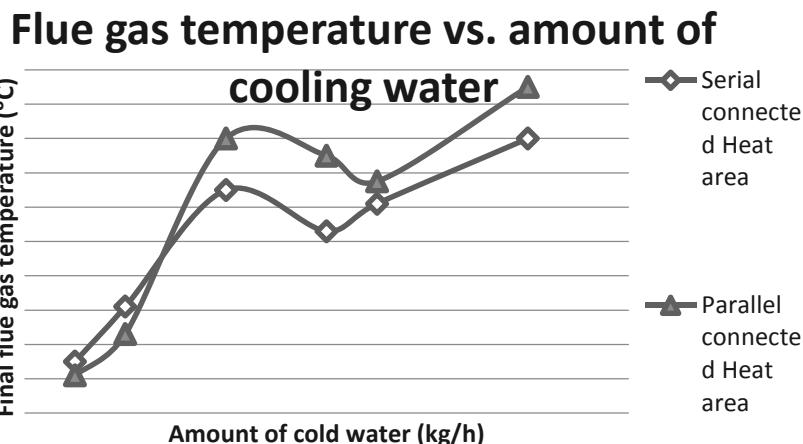


Figure 4. Optimal amount of cold water and optimal heat exchange area

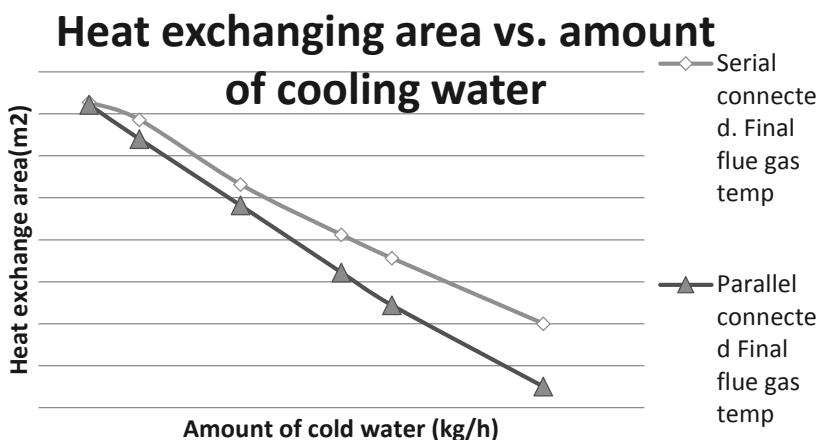


Figure 5. Optimal amount of cold water and optimal heat exchange area

Table 4. Simulated values of composition of ash and aqueous waste produced

Stream Aqueous Waste			
Component	Flow rate (kg/h)	Mass Comp (%)	Conc. g/L
Ash	0.00004	0.0006	0.000025
Ca Hydroxide	16.26015	10.0166	10.602511
Ca Chloride	2.51176	1.5473	1.637806
CaSO ₄	12.97966	7.9957	8.463450
Oxygen	9.04513	5.5720	5.897921
Water	121.53557	74.8684	79.247875
HCl	0.00145	0.0001	0.000765
Ash stream (at 1000 °C)			
	37.53		

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Centar za arhitekturu i urbanizam - CAU je nastao kroz proces intenzivne, međunarodne, intelektualne i profesionalne saradnje na razmjeni ideja između pojedinaca koji su okupljeni oko zajedničkih ciljeva. Pokazalo se da u uslovima globalizacijena i vrijednosti informacije, timski rad umreženih pojedinaca sa raznih krajeva svijeta postaje trend u ozbiljnim projektima. U sveukupnoj klimi prostornog planiranja u Crnoj Gori danas, regionalna i međunarodna saradnja, multidisciplinarnost, nesmetan protok znanja i kapitala, studiozan pristup, zaštita životnog okruženja, održivi razvoj, obnovljiva energija i sl. samo su neke od 'ključnih riječi' za definisanje ispravnog pristupa ovoj ozbiljnoj disciplini. CAU posjeduje licence za izradu prostorno-planske dokumentacije.

AKTIVNOSTI

- prostorno planiranje i urbanizam
- arhitektura i uređenje pejsaža
- saobraćaj i infrastruktura
- investicioni projekti
- studijska istraživanja



**NOVO!!!****NOVO!!!****NOVO!!!**

AD "POLIEX", BERANE

Izgrađen kao fabrika namjenske industrije za potrebe Vojske AD "POLIEX" je prvobitnu proizvodnju minsko-eksplozivnih sredstava je 1991. godine dopunio proizvodnjom inicijalnih sredstava, a tri godine kasnije usvojena je i proizvodnja eksploziva za civilnu upotrebu.

Fabrici je uveden ISO 9001 standard- Sertifikovani sistem menadžmenta i svi proizvodi su usklađeni sa evropskim standardima tj. posjeduju CE znak po tipu Modula B i Modula D.

Fabrika se takođe bavi uslugom minerskog servisa, kao i delaboracijom minsko-eksplozivnih sredstava i ima obučeni kadar i mogućnost da ovu oblast dodatno usavršava.

TERMOBARIK

- Moćnija eksplozivna akcija!!!
- U velikom se opsegu čuvaju svojstva dodatnih razornih činilaca - šrapneli i brizantnost.
- Termobarik municija je fatalna za život u vještačkim i prirodnim skloništima.
- Dizajn termobarik municije blago se razlikuje od konvencionalne municije.
- Veliki broj municije može se pretvoriti u termobarik bez mijenjanja dizajna (avio-bombe).

**Uporedni testovi mine 82 mm
napunjene sastavom TBS i TNT**

**TBS 1****TNT**

**Uporedni testovi punjenja TBS 1 i TNT
mase 2 kg u vodi na dubini od 1 m
TNT ekvivalent TBS-1 minskog dejstva 2.5**

**TBS 1****TNT**

**NOVO!!!****NOVO!!!****NOVO!!!****AMONIJUM PERHLORAT NH_4ClO_4**

Bijeli kristalni prah.Zbog svojih svojstava masovno se koristi u proizvodnji kompozitnih raketnih goriva, a takođe i u pirotehnici.

KALIJUM PERHLORAT KClO_4

Bijeli kristalni prah.Zbog svojih svojstava koristi se eksploziva, posebno u proizvodnji privrednih eksploziva, kao i u pirotehnici.

KALIJUM HLORAT KClO_3

Bijeli kristalni prah.Veoma jak oksidans, koji nalazi široku primjenu u pirotehnici.

KALIJUM NITRAT KNO_3

Bijeli kristalni prah.Veoma široka primjena u mnogim oblastima, posebno u pirotehnici i proizvodnji mineralnih đubriva.

BARIJUM NITRAT $\text{Ba}(\text{NO}_3)_2$

Bijeli kristalni prah.Nalazi primjenu u pirotehnici, naročito za bojenje plama.

BARIJUM HROMAT BaCrO_4

Žuti kristalni prah.Široka primjena u mnogim granama, naročito u pirotehnici.

BARIJUM PEROKSID BaO_2

Sivo bijeli kristalni prah.Zbog izraženih oksidacionih svojstava koristi se u pirotehnici, ali i za dobijanje kiseonika.

OLOVOFEROCIJANID $\text{Pb}_2[\text{Fe}(\text{CN})_6]$

Svjetložuti kristalni prah.Osnovna primjena je pirotehnika.

OLOVO HROMAT PbCrO_4

Žuti do žutocrveni kristali.Upotrebljava se u pirotehnici, ali i u proizvodnji mineralnih boja.

STRONCIJUM NITRAT $\text{Sr}_2(\text{NO}_3)_2$

Bijeli kristalni prah.Upotrebljava se u pirotehnici, ali i u mnogim drugim granama industrije.

SREBRO JODID AgJ

Svjetložuti kristalni prah.Upotrebljava se u fotografiji i kod izrade protivgradnog reagensa, kao aktivna komponenta.

AMONIJUM JODID NH_4J

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Police bb**

Tel/Fax 382 (0)51 241-634

Mob.+382 (0)69 318-211 ; +382 (0)67 444-999



TÜV - 1008

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Analizom i kontrolom različitih segmenta životne sredine doprinosimo njenoj zaštiti i unapređenju. Kontrolom kvaliteta i bezbjednosti hrane doprinosimo podizanju kvaliteta života.

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Centar za ekotoksikološka ispitivanja Podgorica DOO (CETI) je osnovala Vlada Crne Gore za vršenje poslova ispitivanja svih segmenata životne sredine: vazduha, vode, mora, zemljišta, flore i faune, klimatskih promjena, jonizujućeg i nejonizujućeg zračenja, buke i vibracije, izrade posebnih toksikoloških studija, analiza i programa za potrebe državnih organa, naučnoistraživačkih ustanova, privrede i građana, kao i poslova kontrole zdravstvene ispravnosti životnih namirnica i predmeta opšte upotrebe.

CETI vrši:

- ekotoksikološka i ispitivanja kvaliteta (fizičko-hemijska ispitivanja i ispitivanje sadržaja radionuklida) svih segmenata životne sredine (vode, vazduha, zemljišta, sedimenta, mora...);
- kategorizaciju otpada;
- ispitivanje otpadnih gasova - emisija;
- ispitivanje radona;
- snimanje „nultog“ stanja potrebnog za izrade studija lokacija i elaborata o procjeni uticaja na životnu sredinu;
- izradu toksikoloških studija, analiza i programa za potrebe državnih organa, naučnoistraživačkih ustanova, privrednih društava i drugih subjekata;
- dozimetrijska mjerjenja, osiguranje i kontrola kvaliteta (QA/QC);
- kontrolu i izdavanje sertifikata za promet roba (hrane i predmeta opšte upotrebe) u uvozu, izvozu i proizvodnji;
- ispitivanje radne sredine (komfor-mikroklimatski uslovi, hemijske i fizičke štetnosti);
- ispitivanje buke i vibracije u radnoj i životnoj sredini;
- pripremu i izradu akta o procjeni profesionalnih rizika zaposlenih sa predlogom mjera za njihovo otklanjanje.

CETI je institucija koja pored visoke stručnosti posjeduje i višegodišnje iskustvo u djelatnosti ekotoksikoloških ispitivanja svih segmenata životne sredine. Od osnivanja je postigao da svoju djelatnost proširi po obimu, vrsti ispitivanja, broju analiza što je rezultiralo i širenjem liste klijenata tj. korisnika usluga. Danas može da ponudi široki spektar analiza koje se rade po savremenim, svjetski priznatim metodama i sa najkvalitetnijom i najpouzdanijom laboratorijskom opremom.

Temelj uspjeha ujedno i prednost CETI jeste angažman svih zaposlenih, spremnost na nove izazove, a sve sa ciljem ostvarivanja zajedničke vizije – da CETI bude institucija prepoznata, u regionu i šire po stručnosti, pouzdanosti analiza, uvijek raspoloživa na tržištu uz konkurentne cijene.

Tokom 17 godina uspješnog poslovanja najznačajniji klijenti CETI su: Elektroprivreda Crne Gore, Kombinat aluminijuma, Termoelektrana Pljevlja, Luka Bar, Brodogradilište Bijela, Agencija za zaštitu životne sredine, Bemax, Cerovo, Porto Montenegro, Tradeunique, Okov, Nivel i dr.



- *O preduzeću*

Preduzeće „MEDIX“ d.o.o. Podgorica osnovano je u oktobru 1998. godine. Zapošljava 4 radnika koji su u stalnom radnom odnosu, a u honorarnom odnosu ima 15-tak radnika.

- *Djelatnost*

Osnovna djelatnost preduzeća je izrada Elaborata procjene uticaja na životnu sredinu, Strateških procjena uticaja, Studija izvodljivosti i Projekata iz oblasti životne sredine.

U svom dugogodišnjem radu ovo preduzeće je uradilo preko 500 Elaborata procjene uticaja, kao i značajan broj Strateških procjena uticaja i Studija izvodljivosti.

Preduzeće okuplja veliki broj stručnjaka iz različitih oblasti koji za pojedine poslove čine multidisciplinarni tim. Svi angažovani stručnjaci imaju veliko iskustvo u izvršavanju poslova iz oblasti životne sredine, tako da je ovo preduzeće jedno od vodećih u pružanju usluga koje se odnose na sferu njegove djelatnosti.

Osim saradnje sa domaćim institucijama i preduzećima, jedan dio aktivnosti preduzeća je vezan i za saradnju sa inostranim partnerima koji se bave problemima životne sredine.

- *O sposobljenosti*

Preduzeće „Medix“ je u svakom pogledu osposobljeno za obavljanje svoje djelatnosti.



CRNOGORSKO DRUŠTVO ZA KOROZIJU, ZAŠTITU MATERIJALA I ZAŠTITU ŽIVOTNE SREDINE

Vlada Martinovića 55
81000 Podgorica
Kontakt tel.: +382 69 311 673
e-mail: cdzm@ac.me
Žiro račun: **550-2855-54**