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ISSN 0350-350X
GOMABN 42, 4, 237-264
Stručni rad / Professional paper
UDK 665.664.23 : 628.492.004.64 : 504.062.4

SANACIJA GUDRONA SPALJIVANJEM RADI ZAŠTITE OKOLIŠA

Sažetak

Kiseli gudron je zauljena otpadna tvar, koja nastaje prilikom kisele rafinacije međuprodukata nafte odnosno rabljenih ulja koncentriranom sumpornom kiselinom. U Sloveniji postoji nekoliko starih deponija kiselog gudrona. Nedavno se odlučilo pristupiti projektu saniranja tih starih nerješenih ekoloških problema. Poslije ispitivanja i nekih drugih postupaka sanacije, sada se odlučilo isprobati mogućnost spaljivanja gudrona. Za naš rad je bilo odlučeno, da se naprave kemijske analize gudrona sa dvije najveće deponije na području grada Maribora, dakle s deponija na Studencima i u Pesnici. Ove dvije lokacije, kao i neke druge manje bi trebale biti idućih godina sanirane. Gudron je dospio na te deponije prije više od 20 godina. Nastao je pri preradi starih ulja postupkom rafinacije sa sumpornom kiselinom, pri čemu se izvuku nezasičeni ogljikovodici, spojevi metala i organski kloridi. Količina otpadnog materijala pri takvoj preradi iznosi od 3 do 10 % od ulaznih količina.Vidi se da postoji razlika između uzoraka, pogotovo glede koncentracije klora, cinka i olova. Kalorične vrijednosti i koncentracije sumpora su slične i one će najodlučnije utjecati na proces izgaranja te na tvorbu produkata.

Najprije je bila obavljena teoretsko - tehnička studija mogućih i za okoliš sigurnih postupaka spaljivanja neobrađenog gudrona. Zbog karakterističnog kemijskog sastava i fizikalnih svojstava gudrona opredijelili smo se za spaljivanje na osnovi dvije različite tehnologije s različitim postupcima obrade dimnih plinova, koje su neophodno potrebne, radi dostizanja nižih emisijskih koncentracija polutanata u odnosu na propisane dozvoljene emisije od EU.

Dobrim planiranjem svih pokusa, dobrim izborom tehnologije spaljivanja i tehnologijom pročišćavanja dimnih plinova te *kvalitetnim izvođenjem pokusa uspjeli smo izvesti spaljivanje gudrona, koji je dao veoma povoljne rezultate. Pogotovo smo zadovoljni, što smo uspjeli sniziti koncentraciju* SO_2 *ispod dozvoljinih granica. Koncentracije* SO_2 *su bile u dimnim plinima pred čišćenjem na nivou* $10g/Nm^3$*, što pokazuje da je gotovo sav sumpor izgorio i napustio primarnu komoru s dimnim plinovima. Sniženje njegove koncentracije se obavilo u dva odnosno tri koraka. Koncentracije teških metala u šljaki pokazuju da je samo manji dio napustio primarnu komoru, što je olakšalo rad naprava za čišćenje plinova.*

1. Uvod

Ekološka svijest svjetske populacije u zadnjem desetljeću izvanredno raste. Globalni trendovi osvještenja rada s otpadom slijede se i u Sloveniji i na području politike, koja prima sve strože zakonodavstvo, i na području znanosti i tehnike, koji imaju zadatak riješiti dane probleme i realizirati projekte. Jedan od tih projekata je sanacija gudronskih jama. U radu su prikazane značajke spaljivanja kiselog gudrona s ciljem smanjenja emisije u okoliš i tehnološki zahtjevi čišćenja dimnih plinova spaljenog kiselog gudrona s jame na Studencih i u Pesnici (okolica grada Maribora, Slovenija).

Spaljivanje je samo jedan od mogućih oblika zbrinjavanja ovog otpada. Neki drugi oblici i tehnologije mogu imati prevelik negativni utjecaj na okoliš ili su samo kratkotrajno rješenje problema. Sadašnje rješenje zbrinjavanja otpada je sa zakonskog i civilizacijskog gledišta potpuno neprihvatljivo i ni na koji način ne može biti ponos tvrtke koja ga je stvorila.

Spaljivanje ima nekoliko prednosti pred ostalim metodama, a ima i slabosti, koje ćemo istovremeno predstaviti.

Glavna svrha koju realiziramo postupkom spaljivanja je uništenje cjelokupne organske tvari. Spaljivanjem smanjujemo količinu otpada najvećom mogućom mjerom. Produkt može biti inertna tvar a ipak ostaje za odlaganje neprihvatljiv, ako ima previše okolišu štetnih tvari. Spaljivanjem rješavamo biološki i fizikalni problem, kemijski je problem pak sređen samo djelomično. Posljednji problem u najvećoj mjeri ovisi o parametrima spaljivanja, specifičnosti ložišta, sastavu otpada, dodatih reagenata i postupcima obrade dimnih plinova.

Spalionica je energetski objekt, koji nam može uz prigodan, energetski bogat otpad služiti kao izvor toplinske energije. Ovu energiju možemo koristiti u tehnološkim procesima ili za komunalno grijanje. Također, toplinsku energiju možemo parnom turbinom i generatorom pretvoriti u električnu energiju, koju koristimo za krajnje potrebe ili prodaju na tržištu.

Dogovorili smo se za pokusno spaljivanje gudrona u spalionici opasnog otpada PUTO Zagreb i u pilot spalionici Fakulteta za strojarstvo iz Maribora i KIV-a iz Vranskog. Obje spalionice su dvokomornog tipa, što znači, da se otpad u primarnoj komori plinificira i djelomično, spali, a u sekundarnoj komori potpuno izogi pri temperaturama iznad 1000 ℃. Dimni plinovi moraju imati vrijeme zadržavana u tim visokim temparaturama dulje od 2 sekunde, kako bi se dostigla potpuna razgradnja opasnih organskih polutanata. Vrijeme zadržavanja i temperatura su istovremeno i zakonski regulirani.

Spalionica PUTO u Zagrebu je rotacijskog tipa. Poslije sagorijevanja u vertikalnoj sekundarnoj komori najprije slijede izmenjivači topline, zatim je četiri stupanjsko čišćenje dimnih plinova. Čišćenje plinova obuhvaća reaktor, filtar za prašinu, katalizator i toranj za pranje dimnih plinova.

Pilot spalionica Fakulteta za strojarstvo iz Maribora i tvrtke KIV iz Vranskog ima klasičnu primarnu komoru sa rešetkom, koja je napravljena na način, da pastozni odpad ne može kliziti kroz nju. Poslije sekundarne komore dimni plinovi najprije idu kroz izmenjivač toplote, onda slijedi polusuha adsorbcija kiselih komponenata iz dimnih plinova, poslije toga su vrečasti filtri za izdvajanje čestica, na kraju ispred dimnjaka je još filtar iz aktivnog ugljena, radi konačnog čišćenja dimnih plinova pri čemu se izdvoje preostale kisele komponente, teški metali, dioksini i furani.

Dobar kvalitet spaljivanja u primarnoj i sekundarnoj komori u vezi s adekvatnim tretmanom dimnih plinova mora omogućiti rad cjelokupnog objekta u skladu sa svim važečim propisima. Pošto imamo u Sloveniji sve propise o zaštiti okoliša usuglašene sa Europskim direktivama, naše su ograničene emisijske vrijednosti apsolutno gledano jako niske. Zbog toga je u prvom redu potrebno odabrati najbolju tehnologiju za spaljivanje, koja producira najmanje emisije te ostatak papela i šljake. Uz to treba odabrati adekvatno čišćenje plinova, koje će omogučit na jednoj strani emisije polutanata u skladu sa propisima, a na drugoj strani ekonomičan rad naprava sa što manje ostataka poslije čišćenja dimnih plinova.

Rezultati mjerenja svih propisanih emisija prikazuju direktno usporedbu dviju tehnologija spaljivanja i obrade dimnih plinova. Pilot spalionicom smo dostigli bolje rezultate, koji su skoro u potpunosti usuglašeni s europskim normama. Problem prevelike koncentracije prašine i teških metala pri uzorku "Pesnica" može se tehnički riješiti manjom investicijom i poboljšanjem efikasnosti sustava za obradu plinova. Analiza šljake je pokazala da je gudron u potpunosti izgorio, što se vidi iz preostatka TOC-a, kojeg je bilo manje od 1 posto. Koncentracije bakra i olova su tako velike, da ovu šljaku nije moguće odlagati na deponiju za inertni otpad, već na odlagalište za neopasni otpad (s obzirom na slovenske propise). Testiranja izluživanjem su pokazala da je izluživanje u dopuštenim granicama.

Glavna slabost spaljivanja otpada je u relativno velikim troškovima izgradnje i rada spalionice. Uz to je potrebno pronaći i primjeren prostor i okolinu, koja će ovakvu spalionicu prihvatiti, te je potrebno osigurati propisan rad spalionice u smislu dostizanja zakonski dopuštenih emisija štetnih tvari u dimnim plinovima i ostataka nakon spaljivanja i čišćenja dimnih plinova.

Alternative spaljivanju kiselog gudrona su predstavljene u različitim varijantama. Nudi se više komercijalnih rješenja, koja poboljšavaju kemijske, fizikalne i biološke parametre otpada, ali trajno problem unatoč svemu ne rješavaju. Osnovni kriteriji kod izbora tehnologije obrađivanja vezani su uz zakonodavstvo i raspoloživa financijska sredstva, od politike tvrtke do pitanja zaštite okoliša. Ovo posljednje u najvećoj mjeri uzrokuje izbor načina rješavanja problema opasnim otpadom.

2. Kemijska analiza i sastav kiselog gudrona

Kiseli gudron je masna otpadna tvar, koja nastaje prilikom kisele rafinacije međuprodukata nafte, odnosno upotrijebljenih ulja s koncentriranom sumpornom kiselinom. Količina otpadnog materijala pri takvoj preradi iznosi od 3 – 10% ulaznih količina.

Uzroci pojave kiselog gudrona su u primjeni koncentrirane sumporne kiseline za postizanje kisele ekstrakcije sredine u procesu dorade pojedinih rafinerijskih produkata. Procesi kod kojih se u rafinerijskoj tehnologiji koristi postupak kisele rafinacije su:

- proizvodnja benzina,
- proizvodnja baznih ulja, kerozina i parafina,
- rerafinacija upotrijebljenih ulja.

Rerafinacija upotrijebljenih ulja tim kiselinskim postupkom imala je cilj regeneraciju početne kvalitete baznih ulja, što je uključivalo uklanjanje nezasićenih ugljikovodika, spojeva metala odnosno organskih klorida koji su se pojavljivali kao posljedica korištenja takvih produkata.

Tablica1: Karakteristični podaci gudrona

	Jedinica	Uzorak "Pesnica"	Uzorak "Studenci"
Hi	MJ/kg	25,4	22,6
T paljenja	°C	230	227
klor	%	0,007	0,337
sumpor	%	6,1	5,9
cink	mg/kg	1000	510
olovo	mg/kg	1400	550
bor	mg/kg	94	49
kadmij	mg/kg	1	1
PCB	mg/kg	0,8	1,2

U Sloveniji postoji nekoliko starih deponija kiselog gudrona. Nedavno se odlučilo pristupiti projektu saniranja tih starih deponija s ciljem zaštite okoliša. Nakon ispitivanja i nekih drugih postupaka sanacije (solidifikacija živim ili gašenim vapnom), sada se odlučilo isprobati mogućnost spaljivanja gudrona. Odlučeno je da se obave kemijske analize gudrona s dva najveća deponija na području grada Maribora, s deponija na Studencima i u Pesnici. Ove dvije lokacije, kao i neke druge manje, trebale bi idućih godina biti sanirane. Gudron je dospio na te deponije prije više od 20 godina. Nastao je pri preradi starih ulja.

Najinteresantniji podaci o materijalu (gudronu) sakupljeni su u tablici 1. Vidi se da postoji razlika između uzoraka, pogotovo u pogledu koncentracije klora, cinka i olova. Kalorične vrijednosti i koncentracije sumpora su slične i one će najodlučnije utjecati na proces izgaranja te na tvorbu produkata.

3. Odgovarajuće tehnologije za spaljivanje gudrona

Za spaljivanje gudrona u svijetu su upotrijebljene najrazličitije tehnologije, ali ih se jako malo pokazalo sigurnim za okoliš i istovremeno ekonomski prihvatljivim. Prva i najjeftinija mogućnost spaljivanja je suspaljivanje u industrijskim ložištima i termoenergetskim objektima. Ova mogućnost se često koristi zbog velikog broja objekata u svim, pa čak i manje razvijenim zemljama. Vlasnici tih objekata su uvijek zainteresirani dobiti na spaljivanje energetski bogat otpad a uz to i dobro zaraditi.

Spaljivanje otpada, a pogotovo opasnog otpada u takvim objektima vrlo je ozbiljan problem, pa je tome potrebno i tako pristupiti. Kod takvog spaljivanja potrebno je imati u vidu da je ložište objekta projektirano za neku specifičnu vrstu energenta, koji u tom prostoru odgovarujeće dobro izgara u skladu sa svim propisima. Tretman dimnih plinova također je prilagođen za projektirano gorivo i tehnološki postupak. Poremećaj kvalitete i vrste goriva remeti kvalitetu izgaranja i cjelokupni proces bi trebalo ponovno optimirati i preraditi ako želimo u tom ložištu paliti i otpad.

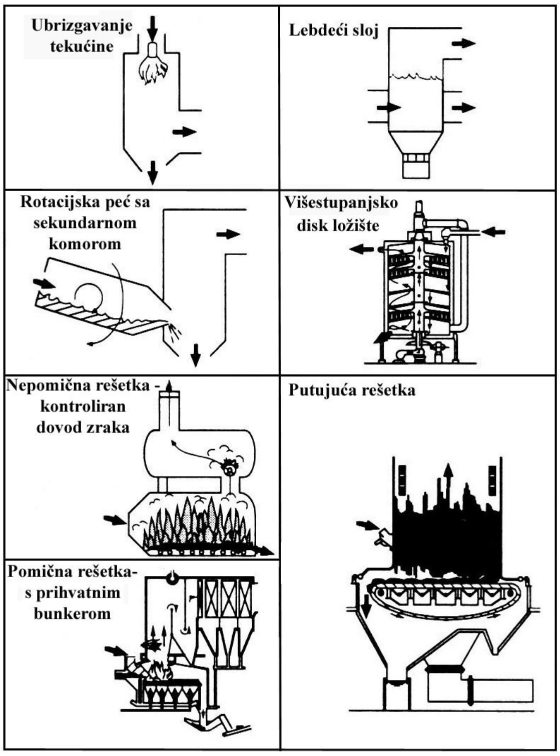
Spalionice otpada a pogotovo spalionice opasnog otpada primarno su sagrađene za tretman otpada. Naravno, ima i razlika između različitih tipova i tehnologija spalionica, ali sve mogu vrlo kvalitetno paliti otpad različitog sastava i različite ogrjevne vrijednosti. Uz to je i napravljen kompletan tretman dimnih plinova, koji izdvaja kisele komponente, teške metale i prašinu. Na taj način je tehnički osiguran siguran rad, jer takav objekt može raditi po propisima najrazvijenih zemalja s vrlo niskim zakonski dopuštenim emisijama polutanata. S toga gledišta za nas je prihvatljiv jedino termički tretman u spalionici opasnog otpada.

Postoji više tehničkih rješenja kako napraviti spalionicu opasnog otpada. Mi ćemo se koncentrirati na objekte u kojima je moguće neopasno spaljivati gudron.

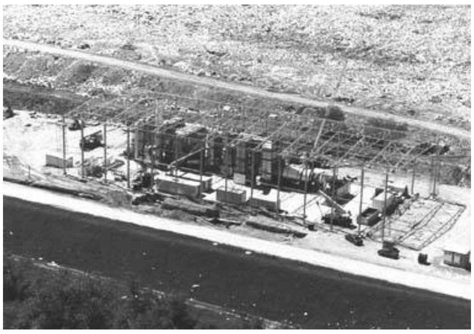
Na slici 1 simbolima su prikazane moguće tehnologije koje bismo mogli upotrijebiti za spaljivanje gudrona. Neke tehnologije su prihvatljivije s gledišta emisija, a neke je moguće izgraditi i s nižim troškovima.

Najprije je bila obavljena teoretsko-tehnička studija mogućih i za okoliš sigurnih postupaka spaljivanja neobrađenog gudrona. Zbog karakterističnog kemijskog sastava i fizikalnih svojstava gudrona (tablica 1) opredijelili smo se za spaljivanje na osnovi dvije različite tehnologije s različitim postupcima obrade dimnih plinova. Obrada dimnih plinova je nužno potrebna radi dostizanja dovoljno niskih emisijskih koncentracija polutanata u odnosu na propisane dopuštene emisije EU.

Slika 1: Nekoliko tehnologija spalionica opasnog otpada (simbol slika)

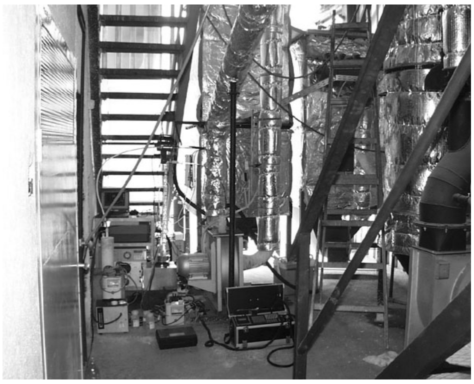


Slika 2: Spalionica PUTO
Figure 2: HWI PUTO



Slika 3: Pilot spalionica
Figure 3: Pilot incinerator

Slika 4: Sustav tretmana dimnih plinova u pilot spalionici
Figure 4: Pilot incinerator flue gas treatment devices

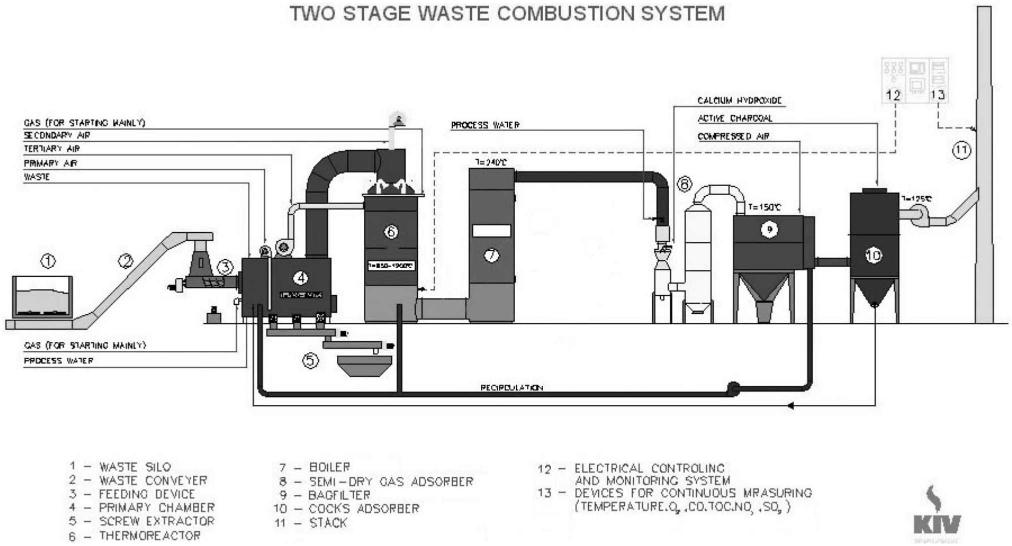


Pokusno spaljivanje gudrona dogovoreno je u spalionici opasnog otpada PUTO Zagreb i u pilot spalionici Fakultete za strojarstvo u Mariboru i KIV-a u Vranskom. Obje spalionice su dvokomornog tipa, što znači da se otpad u primarnoj komori plinoficira i djelomično spali, a u sekundarnoj komori potpuno izgori pri temperaturama iznad 1000℃. Dimni plinovi u sekunda rnoj komori moraju se zadržavati na tim visokim temparaturama duže od 2 sekunde, kako bi se dostigla potpuna razgradnja opasnih organskih polutanata. Vrijeme zadržavanja i temperatura su istovremeno i zakonski propisani, kako bi se već pri projektiranju predvidio odgovarajući oblik i veličina, te upotrijebile komponente za dostizanje tih uvjeta.

Spalionica PUTO (slika 2) u Zagrebu je rotacijskog tipa. Nakon izgaranja u vertikalnoj sekundarnoj komori najprije slijede izmjenjivači topline, a zatim četverostupanjsko čišćenje dimnih plinova. Čišćenje plinova obuhvaća reaktor, filtar za prašinu, katalizator i toranj za pranje dimnih plinova.

Pilot spalionica (slika 3) Fakulteta za strojarstvo iz Maribora i poduzeća KIV iz Vranskog ima klasičnu primarnu komoru s rešetkom, koja je sačinjena tako da pastozni otpad ne može kliznuti kroz nju. Nakon sekundarne komore dimni plinovi najprije idu kroz izmjenjivač topline, nakon čega slijedi polusuha adsorpcija kiselih komponenata iz dimnih plinova, pa vrećasti filtri za izdvajanje čestica, a na kraju ispred dimnjaka još je filter od aktivnog ugljena, radi konačnog čišćenja dimnih plinova pri čemu se izdvoje preostale kisele komponente, teški metali, dioksini i furani (slika 4).

Slika 5: Shema kompletne pilot spalionice
Figure 5: Schematic presentation of complete pilot incinerator



Na slici 5 je prikazana shema cijelog sustava spaljivanja i obrade plinova pilot spalionice.

Dobra kvaliteta spaljivanja u primarnoj i sekundarnoj komori osigurava relativno nisku količinu polutanata. Zbog sastava otpada još je uvijek potreban podesan tretman dimnih plinova, koji mora omogućiti rad cjelokupnog objekta u skladu sa svim važećim propisima. Budući da u Sloveniji imamo sve propise o sigurnosti okoliša usuglašene s europskim pravilima, naše su ograničene emisijske vrijednosti, apsolutno gledano, vrlo niske. Zbog toga je u prvom redu potrebno odabrati najbolju tehnologiju za spaljivanje, koja proizvodi niske količine emisije te ostatke pepela i šljake. Uz to je potrebno odabrati odgovarajuće čišćenje plinova, koje će omogućiti emisiju polutanata u skladu s propisima i ekonomičan rad naprava sa što manje ostataka nakon čišćenja dimnih plinova. Sve što preostaje nakon spaljivanja ponovno je otpad kojeg treba uz poznate troškove i ukloniti.

4. Mjerenje emisija i analiza pepela i šljake

Rezultati mjerenja svih propisanih emisija, čije su vrijednosti prikazane u tablici 2 pokazuju direktno usporedbu dvije različite tehnologije spaljivanja i obrade dimnih plinova. Najprije je obavljeno spaljivanje u spalionici PUTO, koje je već pokazalo relativno velike emisije polutanata, koje smo a osnovi analize i očekivali (vidi tablicu 1). Ponajviše to važi za emisije sumpornog dioksida, vodikovog klorida i teških metala. Emisija dioksina i furana se u PUTU nije mjerila. Zabrinjavajuće je djelovanje, da čak ni tretman dimnih plinova u četiri stupnja nije uspio pročistiti dimne plinove ispod propisane granice. Inače je samo spaljivanje prošlo bez problema i gudron je dobro i brzo izgorio. U PUTU su se istovremeno spaljivali uzorci "Pesnica" i "Studenci".

Tablica 2: Prosječne dnevne emisije u zrak iz spalionice

Parametar	Direktive 2000/76/EC - europska direktiva za spalionice i SLO legislativa	Spalionica PUTO Zagreb (prosječna emisija za oba uzorka)	Pilot spalionica FS-MB & KIV, Uzorak Pesnica	Pilot spalionica FS-MB & KIV Uzorak Studenci
Skupna prašina	**10**	91	22	14
CO	**50**	138	38	17
TOC	**10**	1	0,7	0,2
SO_2	**50**	1430	16	50
NO_x	**200**	109	78	77
HCl	**10**	114	12	5,9
HF	**1**	2,2	0,41	<0,1
Cd, Tl – zajedno	**0,05**	0,0008	0,00021	0,00002
Hg	**0,05**	0,002	0,00008	0,00004
Ag, Sb, As, Pb, Cr, Co, Mn, Ni, V, Sn – zajdno	**0,5**	0,75	0,89	0,041
PCDD/F	**0,1**	-	<0,05	<0,05

Napomena: Sve koncentracije su izražene u [mg/Nm^3], jedino PCDD/F je izražen u [ng TE/m^3]

Kod paljenja u pilot spalionici na Vranskom su se odvojeno spaljivali uzorci. Počeli smo s uzorkom "Pesnica" a završili sa uzorkom "Studenci". Na osnovu analize gudrona i problema u PUTU još je bolje pripremljen postupak tretmana dimnih plinova a dodao se i sustav "in-situ" za dodavanje vapna u samo ložište, kako bi se već kod spaljivanja smanjila koncentracija sumpora u dimnim plinovima. Variranjem rada sustava "in-situ" i prilagođavanjem sustava tretmana uspjelo se doći do rezultata, koji su predstavljeni u tablici 2.

Uočljivo je da smo pilot spalionicom postigli bolje rezultate, koji su gotovo u potpunosti usuglašeni s europskim normama. Problem prevelike koncentracije prašine i teških metala pri uzorku "Pesnica" može se tehnički riješiti manjom investicijom i poboljšanjem efikasnosti sustava za obradu plinova.

Tablica 3: Analiza šljake od spaljivanja gudrona
Table 3: Analysis of slag from gudron incineration

Parametar/Parameter	Jedinica/Unit	Legislativa SLO Regulation SLO	Analiza šljake Slag analysis
TOC	%	3	< 1
CH	mg/kg	2500	< 20
PCDD/F	ng/kg	-	< 1
Al	%	-	0,7
Ba	mg/kg	-	370
Cu	mg/kg	500	520
Zn	mg/kg	1500	5200
Cd	mg/kg	12	3
Cr	mg/kg	500	100
Co	mg/kg	250	< 20
Mn	mg/kg	-	360
Ni	mg/kg	500	150
Pb	mg/kg	500	3900
V	mg/kg	-	20
Fe	%	-	3

Tablica 4: Analiza izluživanja šljake
Table 4: Slag leaching test results

Parametar	Jedinica	Legislativa SLO	Izluživanje
pH		5,5 - 13	12
TOC	mg/l	-	< 5
KPK	mg/l	-	400
AOX	mg/l	1,0	0,03
Ba	mg/l	10	0,1
Cu	mg/l	10	< 0,1
Zn	mg/l	10	0,4
Cr (6 val.)	mg/l	5	< 0,01
Pb	mg/l	2,0	< 0,05
N	mg/l	200	1,7
F	mg/l	20	0,3
V	mg/l	2,0	0,02
SO_4	mg/l	-	2500

Analiza šljake (tablica 3) u pilot spalionici nakon spaljivanja oba uzorka pokazala je da je gudron u potpunosti izgorio, što se vidi iz preostalog TOC-a, kojeg je bilo manje od 1%. Za odlaganje na deponiju još je jako važna koncentracija teških metala. Analiza je pokazala, da su koncentracije bakra i olova tako velike da ovu šljaku nije moguće odlagati na deponiju za inertni otpad, već na odlagalište za neopasni otpad (s obzirom na slovenske propise).

Količine svih ostalih metala nisu problematične za deponiranje.

Analizi šljake potrebno je dopunsko izvoditi i testiranja s izluživanjem, kako bi se ustanovila prikladnost za odlaganje na odgovarajući deponij. Rezultati testova su prikazani u tablici 4 i kažu, da je izluživanje svih parametara u dopuštenim granicama.

5. Sustav "In-situ" u kombinaciji sa sustavom tretmana dimnih plinova u tri stupnja

Potrebno je naglasiti da su se za vrijeme spaljivanja tražili najpovoljniji režimi "in-situ" sustava i sustava tretmana dimnih plinova, kako bi se dostigle najniže emisije polutanata uz najmanju količinu ostatka nakon spaljivanja i najmanju potrošnju aditiva. Koncentracije SO_2 bez dodavanja vapna su bile u dimnim plinovima pred čišćenjem na razini 10g/Nm^3, što pokazuje, da je gotovo sav sumpor izgorio i napustio primarnu komoru s dimnim plinovima.

O sastavu otpada već je bilo govora kad smo predstavili detaljnu kemijsku analizu. Vidi se da je element koji producira najveće količine štetnih emisija sumpor, koji je u otpadu prisutan kao:

- pirit (sulfid) – anorganski spoj sumpora (npr: FeS_2) - anorganska kiselina,
- organsko vezan sumpor za C_nH_m molekule – organske kiseline,
- sulfat – iz njega se može sumpor osloboditi samo kod visokih temperatura,
- elementarni sumpor.

Nešto sumpora možemo poslije spaljivanja pronaći i u pepelu. Obično možemo očekivati oko 95% konverziju sumpora i sumpornih spojeva u plinu, osim sumpora, koji je vezan u sulfatima. Otpad koji ima čistu sumpornu kiselinu, lako uzrokuje formiranje SO_3 kod spaljivanja.

Na pilot spalionici je bilo najprije obavljeno čišćenje dimnih plinova u tri stupnja sljedećim redoslijedom:

- polusuha adsorpcija,
- vrećasti filtar i
- koks adsorber.

<u>Polusuha adsorpcija</u> izvršena je uporabom kalcijevog hidroksida, hidratiziranog vapna, ($Ca(OH)_2$ + voda). Uz pomoć raspršivača u smjeru toka injektira se u reaktor. Alkalno vapneno mlijeko je reagiralo i neutraliziralo kisele komponente u dimnim plinovima. Pri tom su nastale razne soli i voda. Na taj način smo uklanjali uglavnom sumporne okside, a uz to i nešto halogenida.

Proces izdvajanja sumpornog oksida kalcijevim hidroksidom se najbolje izvodi kod temperatura između 200 i 250°C po sljedećoj reakciji:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_4 + H_2O$$

Zbog navedenih svojstava je uporaba kalcijeveg hidroksida najbolja u adsorberima.

<u>Vrećasti filtar</u> izdvaja čestice koje stižu s dimnim plinovima iz ložišta i djeliće, koji nastanu kod polusuhe adsorpcije. Čišćenje vrećastih filtra izvodi se pneumatski.

<u>Koks</u>, proizveden iz ugljena, služi kao treći stupanj čišćenja. Njime je pokriven pretočni presjek reaktora, tako da svi dimni plinovi putuju kroz njega. Koks adsorber služi kao polirni stupanj čišćenja dimnih plinova kojim izdvajamo iz plinova kisele komponente, teške metale, spojeve ugljikovodika, čestice, dioksine i furane.

Kod reguliranja kiselih emisija sustavom "in-situ" u samo se ložište (primarnu komoru) dodaje kalcijev oksid ili vapnenac i na taj način osigurava "in-situ" izdvajanje sumpora. U ložištu reagira živo vapno ili vapnenac sa sumporom, koji se u velikim količinama nalazi u kiselom gudronu. Na taj način se već kod spaljivanja gudrona osigura vezivanje sumpora u kalcijev sulfat. Tako se koncentracija sumpora u neobrađenim dimnim plinovima smanji čak i do pet puta. Uz takvo rješenje je rad naprave za čišćenje dimnih plinova manje zahtjevan pa ga je moguće bolje obaviti.

Uporabu vapnenca ($CaCO_3$), kalcijevega karbonata, možemo predstaviti sljedećim reakcijama:

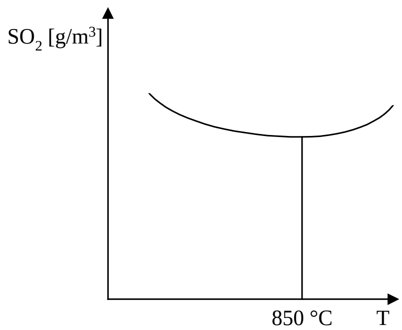
$$CaCO_3 \rightarrow CaO + CO_2 \text{ – kalcinacija}$$

$$CaO + SO_2 \rightarrow CaSO_3$$

$$\left.\begin{array}{l} CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4 \\ CaO + SO_3 \rightarrow CaSO_4 \end{array}\right\} \text{kalcijev sulfat (gips)}$$

Slika 6: Optimalno temperaturno područje za dodavanje vapnenca

Figure 6: Optimal temperature range for lime admix



U tom primjeru proces kalcinacije povećava koncentraciju CO_2 u komori izgaranja, što je loše za spaljivanje. Optimalno temperaturno područje za gornje reakcije je između 800 i 850°C. Količina vapnenca zavisi od molskog omjera Ca/S. Uz to ima velik utjecaj i vrsta vapnenca (meki je bolji).

Ako dodajemo u prostor za izgaranje kalcijev oksid (CaO), onda važi sljedeća reakcija:

$$CaO + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4$$

Na takav način smo u praksi za vrijeme pokusnog spaljivanja smanjili koncentraciju SO_2 sa oko 10 g/m^3 na oko 3 g/m^3. Kod toga je nastala odgovarajuća količina sadre ($CaSO_4$), što računski predstavljamo na osnovi stehiometrije:

$$1 \text{ mol } SO_2 \rightarrow 1 \text{ mol } CaSO_4$$

$$m_{CaSO_4} = 2{,}125 \cdot m_{SO_2}$$

Sada možemo zapisati sljedeću zavisnost kod izgaranja gudrona: 1 kg gudrona → 12 m^3 dimnih plinova, koju izračunamo iz sljedećeg omjera izmjerenih parametra:

- prosječna emisija SO_2 iz neobrađenih dimnih plinova iznosi 10 g/m^3,
- kilogram gudrona ima s obzirom na analize oko 60 g sumpora (tablica 1).

Kada spalimo kilogram gudrona, proizvedemo u skladu sa stehimetrijskom jednadžbom iz 60 grama sumpora 120 g sumpornog dioksida:

$$S + O_2 \rightarrow SO_2,$$

što iznosi 12 m^3 dimnih plinova na 1 kilogram gudrona.

Ako smanjimo koncentraciju SO_2 s 10 na 3 g/m^3, znači da sukladno sa stehiometrijskim računom proizvedemo 178 g $CaSO_4$ na kilogram gudrona. Ako uzmemo u obzir još stupanj iskorištenja, koji je oko 75 %, možemo očekivati oko 240 g sadre. Ako tome ostatku dodamo još oko 100 g pepela na kilogram gudrona, ostaci poslije spaljivanja u komori izgaranja tom metodom iznosit će između 30 i 35 % količine gudrona.

Ovaj postupak dovođenja živog vapna ili vapnenca u komoru za izgaranje može negativno utjecati na proces izgaranja u primarnoj komori, jer pokrije paleći sloj kiseloga gudrona i tako onemogućuje dovod zraka s gornje strane do gudrona i posljedične reakcije izgaranja na površini. Zbog toga je potrebno dodavati više dodatnog goriva, da se osigura odgovarajuća temperatura za poli-pirolitičnu plinofikaciju, koja se vrši u primarnoj komori.

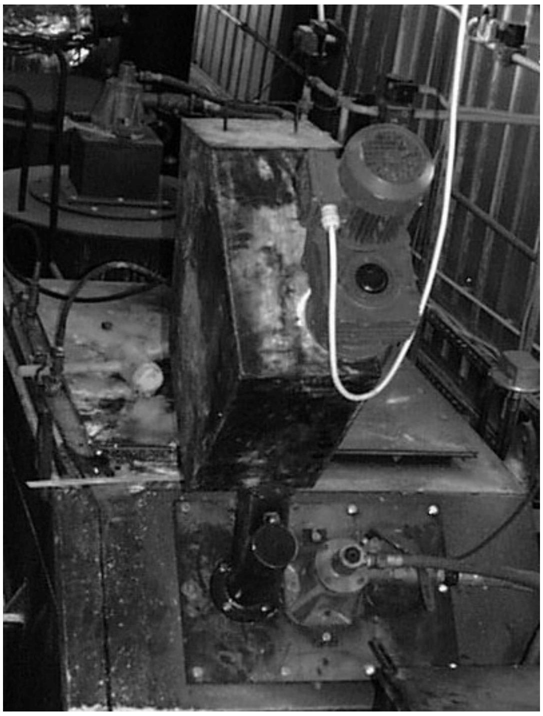
Za takav postupak je bitna i temperatura u primarnoj komori. Ako ona prijeđe 1000°C, reakcija izlučivanja SO_2 se okrene i kalcijev sulfat se počinje razgrađivati:

$$2\, CaSO_4 \rightarrow 2\, CaO + 2\, SO_2 + O_2$$

Velik utjecaj na kvalitetu uklanjanja sumpora iz dimnih plinova ovim postupkom dovođenja aditiva u primarnu komoru izgaranja ima kvaliteta i količina dovedenog aditiva. Za vrijeme pokusa bilo je utvrđeno, da je nužno osigurati dobru podjelu aditiva po komori za izgaranje, koji mora biti za znatno smanjenje koncentracije sumpora u dimnim plinovima ravnomjerno podijelen cijelom komorom izgaranja u odgovarajućoj količini. Premalene količine aditiva ili slaba podjela ne daje povoljni učinak smanjenja koncentracije sumpora u dimnim plinovima, prevelike koncentracije pak previše "gase" spaljivanje gudrona, što znači gubitak materijala kojeg je potrebno nabaviti i nepotrebno veće količine ostataka nakon spaljivanja.

Slika 7: Uređaj za dovod kalcijeveg oksida u primarnu komoru

Figure 7: Device for calcium oxide admix into primary chamber



Slika 7 prikazuje jednostavan sustav za dodavanje aditiva u primarnu komoru pilot spalionice. Izrađen je bio specijalno za pokusno spaljivanje gudrona. Količina dovedenog živog vapna je bila regulirana sekvencnim regulatorom, koji je bio programski vezan na ostale procesne parametre primarne komore. Za vrijeme pokusa bilo je izvedeno više varijanti količina i oblika dodavanja živog vapna.

5. Zaključci

Dobrim planiranjem svih pokusa, pogodnim izborom tehnologije spaljivanja i tehnologijom pročišćavanja dimnih plinova, te kvalitetnim izvođenjem pokusa uspjeli smo izvesti spaljivanje gudrona, koji je dao vrlo povoljne rezultate, koji mnogo obećavaju. Pogotovo smo zadovoljni što smo uspjeli sniziti koncentraciju SO_2 ispod dopuštenih granica. Koncentracije teških metala u šljaci pokazuju da je samo manji dio napustio primarnu komoru, što je olakšalo rad naprava za čišćenje plinova.

Analiza svih rezultata pokazuje da je spaljivanje tehnologija, koju je moguće upotrijebiti za tretman kiselog gudrona. Sve emisije u okoliš koje su iznad dopuštenih koncentracija mogu se manjim naporom sniziti ispod dopuštenih vrijednosti. Kod kemijske analize i testa izluživanja šljake pokazalo se, kako ima u njoj nekih teških metala u prevelikoj koncentraciji, da bi se šljaku moglo odložiti na deponij za inertni otpad, gdje je odlaganje i najjeftinije.

Tretman kiselog gudrona spaljivanjem je sanacija, koju je moguće izvesti u skladu s važećim lokalnim i europskim pravilima i predstavlja konačno i trajno rješenje s minimalnim utjecajem na okoliš za vrijeme tretmana.

ENVIRONMENTALLY SAFE REMEDIAL OF ACID SLUDGE BY INCINERATION

Abstract

Acid sludge or gudron is oily waste that forms in the process of acid rafination inter products of crude oil or waste oil with concentrated sulphur acid. There are several old dump sites for acid gudron in Slovenia. Recently was made a decision to start the remedial process of these old unsolved ecological problems. After the recent investigation of some other remedial processes, a decision was made to investigate the incineration of acid sludge. In order to conduct the investigation, chemical analyses of acid sludge from two biggest dump sites in area of the city of Maribor, located in the city suburbs of Studenci and Pesnica was made. These two locations and several smaller will be in remedial process in the course of next years. Gudron was transported there more then 20 years ago. It was produced while processing old oils with the process of rafination with sulphur acid. With this process the unsaturated hydrocarbons, metal parts and carbon chlorides are removed. The amount of waste *material in such a process is between 3 and 10 percent of input quantity. There is a difference between the two samples, especially in concentration of chlorine, zinc and lead. Calorific value and concentration of sulphur are similar and they are the most influential in the process of combustion and formation of combustion products.*

In the very beginning, the theoretical-technical study of possible and environmentally safe processes of incineration of unprocessed acid sludge was conducted. Due to specific chemical composition and physical properties of acid sludge the decision was made to perform test incineration of acid sludge by using two different technologies with variety of flue gas treatment systems, which are indispensably necessary for reaching the flue gas emission levels set by the European Community Directive.

Appropriate planning of all test trials with correct selection of incineration technology and technology of flue gas treatment together with precise execution of tests shows, that it is possible to incinerate acid sludge with very good results. The concentration of SO_2 was the hardest to get under the legislative value. The SO_2 concentration in raw gases was around 10 g/Nm^3, showing that all sulphur has been burnt and has left the primary combustion chamber with flue gases. The reduction of its concentration was undertaken in two or in three steps. The concentration of heavy metals in slag shows, that only smaller part of them has left the primary chamber, adding to the eased work of flue gas treatment devices.

1 Introduction

Environmental concern of world population is in remarkable increase in recent decade. Global trends on the field of waste processing are monitored also in Slovenia. Changes concern the field of politics that introduces tougher regulations and field of science and technology that has to solve the arisen problems and carry out projects. One of these projects is the remedial of gudron sites. In this paper environmental aspects of acid gudron incineration and technology demands for flue gas treatment of incinerated acid gudron from dump sites Studenci and Pesnica (Maribor city surroundings, Slovenia) are presented.

Incineration is only one of possible technologies for treating this waste. Some other technologies of this waste remedial might have too extensive negative impact on environment or do not solve the problem of waste permanently. Present solution for this waste is totally unacceptable from legislative as well as from civilisation standpoint and can not represent a positive image for the company that produced the waste.

Incineration has several advantages in comparison to other technologies but it has also certain drawbacks. All of them will be presented herein.

Main aim of the incineration is thermal destruction of all organic matter. Incineration enables highest reduction of waste among available technologies. Incineration products are slag and ash, material that can be unsuitable for environment if it has to much dangerous components for the environment. Incineration solves the organic and physical problem of the waste and inorganic part is solved only partly. The later depends highly on the combustion parameters, properties of furnace, waste composition, added reagents and methods of flue gas treatment.

Incinerator is an energetic plant. With suitably calorific ware it can be used as heat energy source. This energy can be used in technological processes, district heating or co-generation of electric energy, that can be used for own needs or sold on the market.

Test incineration of acid sludge was conducted in hazardous waste incinerator PUTO in Zagreb and in pilot incinerator of Faculty of mechanical engineering from Maribor and KIV from Vransko. Both incinerators have two stage technology, meaning that in first combustion chamber the waste gasifies and partly combusts, while in secondary combustion chamber waste completely combusts at the temperatures over 1000 °C. Residence time of flue gases in these high temperatures has to be longer than 2 seconds in order to achieve complete destruction of hazardous organic pollutants. Residence time and temperature are duly defined in the legislation.

Hazardous waste incinerator PUTO in Zagreb has a rotary kiln. After combustion of gases in vertical secondary chamber the flue gases first enter the heat exchanger, then they enter the four stage flue gas cleaning. The cleaning consists of reactor, dust filter, catalyst and tower for washing the flu gases.

Pilot incinerator of Faculty of Mechanical Engineering from Maribor and company KIV from Vransko has a standard primary chamber with specially designed grate not permitting solid or pasty waste to slip through it. After combustion in secondary chamber the flue gases enter the heat exchanger and then enter the system of semi dry adsorption of acid components in flu gases, then they pass through bag filters for particles removal and before going out the chimney they go through active coke filter for final cleaning, where the remaining acid components, heavy metals, dioxins and furans are removed.

High quality incineration in primary and in secondary chamber in combination with appropriate flue gas treatment should assure the operation of the whole plant in order with legislative demands. Since Slovenian legislation of environmental protection is already harmonised with European Union Directives, our legislation emission levels are very low. Having this in mind, a primary need is to find the technology of incineration, that produces small amounts of gas emissions and residual of ash and dust. Additionally there is a need to find proper flue gas treatment, which will on one hand enable emissions of flue gases under legislative values and on other hand guarantee an economical work of treatment devices with as less as possible remainings after flue gas treatment.

Measurement results of all legislatively defined emission values show direct comparison of two technologies of incineration and flue gas treatment. Better results were produced with pilot incinerator, which are almost completely comparable with the standards of European Directive. The exceeded concentration of dust and heavy metals at sample "Pesnica" can be technically solved with smaller investment and improvement of efficiency of flue gas treatment devices. The slag analyses show the total burn out of acid sludge. This can be seen from concentration of the remaining TOC, that was lower than 1 percent. Amounts of copper and lead in the slag are so high, that this slag can not be deposited on refuse dump for inert waste. Instead, in accordance with Slovenian legislation, it has to be deposited on waste bump for non hazardous waste. Conducted leaching test showed all concentrations under legislative values.

Main disadvantage of waste incineration is relatively high investment and operational cost. Additionally proper location needs to be found for incinerator. The waste incineration process must be in accordance with legislation and operate below limit values for air pollutant emissions and remains after incineration and flue gas treatment.

There is variety of alternative options towards the acid gudron incineration. Several technologies are commercially available and improve chemical, physical and biologic properties of waste but do not permanently solve the problem of waste and additionally magnify total mass of waste. Basic criteria for selection of technology for hazardous waste treatment are the legislation and available finance resources, company strategy and environmental awareness of leadership. The later is the most influential decision making factor for hazardous waste technology selection.

2 Chemical analysis and composition of acid sludge

Acid sludge is oily waste that forms in the process of acid rafination of inter products of crude oil or waste oil with concentrated sulphur acid. The amount of waste material with this technology is from 3 to 10 percent of input quantities.

Acid sludge was formed with use of concentrate sulphuric acid for forming acid extraction media in the process of completion of separate refinery products. Acid rafination was in refinery technology used for:

- production of benzene,
- production of base oils, kerosene and paraffin,
- rerafination of used oils.

The object of rerafination of used oils with this acid technology was regeneration of initial quality of base oils. With this process the unsaturated hydrocarbons, metal parts and carbon chlorides that entered the oil while in use are removed.

There are several old dump sites for acid gudron in Slovenia. Recently a decision was made to start the remedial process of these persistent, unsolved ecological problems. After the recent investigation of some other remedial processes (solidification with unslaked or slaked lime), a decision was made to investigate the incineration of acid sludge. In order to conduct the investigation, chemical analyses of acid sludge from two biggest dump sites in area of the city of Maribor, located in the city suburbs of Studenci and Pesnica was made. These two locations and several smaller will be in remedial process in the course of next years. Acid sludge was transported there more then 20 years ago. It was produced while processing old, used oils.

Most interesting data on waste material (gudron) is presented in Table 1. As illustrated in the presented data, there is a difference between the two samples, especially in concentration of chlorine, zinc and lead. Calorific value and concentration of sulphur are similar and they are the most influential in the process of combustion and formation of combustion products.

Table 1: Characteristic data of acid sludge

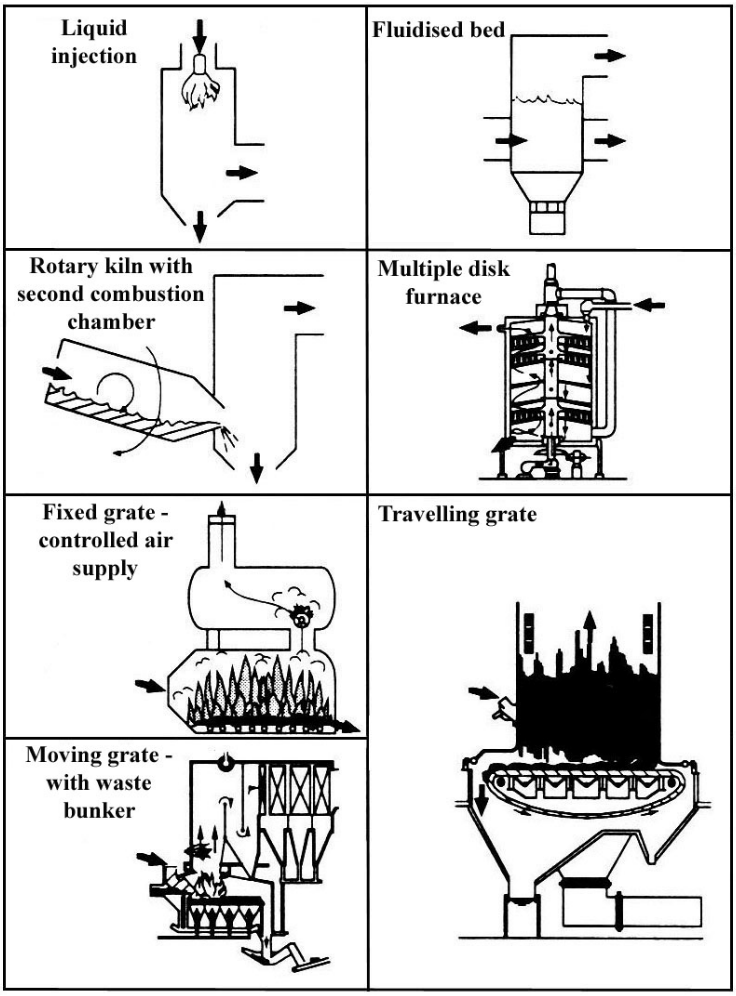
	Unit	Sample "Pesnica"	Sample "Studenci"
Hi	MJ/kg	25,4	22,6
T ignition	°C	230	227
chlorine	%	0,007	0,337
sulphur	%	6,1	5,9
zinc	mg/kg	1000	510
lead	mg/kg	1400	550
boron	mg/kg	94	49
cadmium	mg/kg	1	1
PCB	mg/kg	0,8	1,2

3 Appropriate technologies for acid sludge combustion

There are several different technologies available for acid sludge incineration but only a few of them have proved to be environmentally safe and economically affordable at the same time. The first and the cheapest possibility of combustion is co-incineration in industrial furnaces and thermal power plants. This form of treatment is commonly in use since there are a great number of plants even in lower developed countries. Plant owners are interested in making lucrative business and therefore tend to accept high calorific waste.

Waste co-incineration and especially hazardous waste co-incineration in these plants is very serious and complicated process and needs to be acceded in this manner. When conducting co-incineration the furnace is not fuelled with projected type of fuel that is best suited for this combustion chamber. Projected fuel easily combusts and forms emissions in accordance with the regulations. At the same time are flue gas treatment devices made for projected fuel and technology. Altering the quality and sort of fuel changes the quality of combustion and the whole process needs new optimisation and modification in order to achieve high quality incineration of waste material in the furnace.

Figure 1: Several hazardous waste incineration technologies (symbolic figure)



Waste incinerators and especially hazardous waste incinerators are primarily made to treat waste. There are substantial differences between different types and technologies of incineration but all of them can treat different waste with different calorific value with very high efficiency. Additional to that there is a complete treatment of flue gases, that removes acid components, heavy metals and dust. This technically ensures environmentally safe operation within regulation limit values of all highly developed countries. Having this in mind the only acceptable treatment of hazardous waste is in hazardous waste incinerator.

Several technical solutions are available in order to make a good hazardous waste incinerator. For the scope of this paper only those are presented that can safely treat acid sludge.

Figure 1 symbolically shows possible technologies that can be used to incinerate acid sludge. Some technologies are more acceptable from the standpoint of low emissions and some can be produced with low cost.

In the very beginning, the theoretical-technical study of possible and environmentally safe processes of incineration of unprocessed acid sludge was conducted. Due to specific chemical composition and physical properties of acid sludge (Table 1) the decision was made to perform test incineration of acid sludge by using two different technologies with variety of flue gas treatment systems. Flue gas treatment devices are indispensably necessary for reaching the flue gas emission levels set by the European Community Directive.

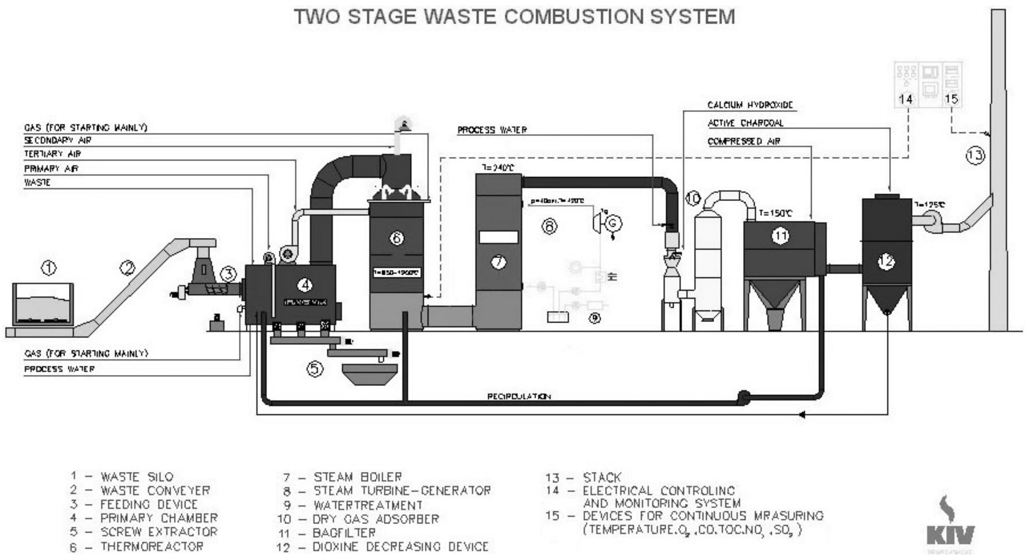
Test incineration of acid sludge was conducted in hazardous waste incinerator PUTO in Zagreb and in pilot incinerator of Faculty of mechanical engineering from Maribor and KIV from Vransko.

Both incinerators have two stage technology meaning that in first combustion chamber the waste gasifies and partly combusts, while in secondary combustion chamber waste completely combusts at the temperatures over 1000 °C. Residence time of flue gases in these high temperatures has to be longer than 2 seconds in order to achieve complete destruction of hazardous organic pollutants. Residence time and temperature are duly defined in the legislation in order to undertake necessary measures already at the planning and designing stage of building new incinerator.

Hazardous waste incinerator (HWI) PUTO (Figure 2) in Zagreb has a rotary kiln. After combustion of gases in vertical secondary chamber the flue gases first enter the heat exchanger and then they enter the four stage flue gas cleaning. The cleaning consists of reactor, dust filter, catalyst and tower for washing the flu gases.

Pilot incinerator of Faculty of Mechanical Engineering from Maribor and company KIV from Vransko has a standard primary chamber with specially designed grate not permitting solid or pasty waste to slip through it. After combustion in secondary chamber the flue gases enter the heat exchanger and then enter the system of semi-dry adsorption of acid components in flu gases, then they pass through bag filters for particles removal and before going out the chimney they go through active coke filter for final cleaning, where the remaining acid components, heavy metals, dioxins and furans are removed (Figure 4). Figure 5 schematically shows complete pilot incinerator with incineration and flue gas treatment devices.

Figure 5: Schematic presentation of complete pilot incinerator



High quality incineration in primary and in secondary chamber ensures low emission of pollutants. Because of the composition of the waste material appropriate flue gas treatment is still needed to assure the operation of the whole plant in order with legislative demands. Since Slovenian legislation of environmental protection is already harmonised with European Union Directives, our legislation emission levels are very low. Having this in mind, a primary need is to find the technology of incineration that produces small amounts of gas emissions and residual of ash and dust. Additionally there is a need to find proper flue gas treatment, which will on one hand enable emissions of flue gases under legislative values and on other hand guarantee an economical work of treatment devices with as less as possible remainings after flue gas treatment. All incineration remains are again wastes that need to be disposed of with appointed costs.

4 Gas emission measurements and analyses of ash and slag

Measurement results of all legislatively defined emission values are presented in Table 2 and show direct comparison of two technologies of incineration and flue gas treatment.

First incineration trials were performed in hazardous waste incinerator PUTO and produced relatively high emissions of pollutants that were anticipated on the knowledge of analyses (Table 1). This is especially true for emissions of sulphuric dioxide, hydrogen chloride and heavy metals. Emissions of dioxins and furans were in PTUO not measured. It is anxious that the standard four-stage flue gas treatment system was not able to treat flue gases below the limit values. Otherwise, the incineration trial has gone through without any problems and acid sludge has burnt out quickly and completely. Both samples ("Pesnica" and "Studenci") were incinerated at the same time in PUTO.

Incineration of both samples in pilot incinerator in Vransko was performed separately. It was started with sample "Pesnica" and finished with sample "Studenci". Based on the acid sludge analyses and emission problems in PUTO there was additional preparation of flue gas treatment devices and "in-situ" system for lime delivery directly into the furnace was added to lower the sulphur dioxide concentration in flue gases. By varying the working properties of "in-situ" system and by adjusting the flue gas treatment devices it was possible to achieve the results presented in Table 2. Details of the "in-situ" system and flue gas treatment devices are presented in chapter 5.

Table 2: Average daily air emissions from incinerators

Parameter	Directive 2000/76/EC – European directive for incinerators and SLO regulation	Incinerator PUTO Zagreb (average emission for both samples)	Pilot incinerator FS-MB & KIV, Sample Pesnica	Pilot incinerator FS-MB & KIV Sample Studenci
Total dust	**10**	91	22	14
CO	**50**	138	38	17
TOC	**10**	1	0,7	0,2
SO_2	**50**	1430	16	50
NO_x	**200**	109	78	77
HCl	**10**	114	12	5,9
HF	**1**	2,2	0,41	<0,1
Cd, Tl - together	**0,05**	0,0008	0,00021	0,00002
Hg	**0,05**	0,002	0,00008	0,00004
Ag, Sb, As, Pb, Cr, Co, Mn, Ni, V, Sn – together	**0,5**	0,75	0,89	0,041
PCDD/F	**0,1**	-	<0,05	<0,05

Note: All concentrations are expressed in [mg/Nm^3], except PCDD/F are expressed in [ng TE/m^3]

Better results were produced with pilot incinerator, which are almost completely comparable with the standards of European Directive. The exceeded concentration of dust and heavy metals at sample "Pesnica" can be technically solved with smaller investment and improvement of efficiency of flue gas treatment devices.

The slag analyses (Table 3) after incinerating both samples in pilot incinerator show the total burn out of acid sludge. This can be seen from concentration of the remaining TOC that was lower than 1 percent. For the final disposal of slag are very important the concentrations of heavy metals. Analyses show that amounts of copper and lead in the slag are so high, that this slag can not be deposited on refuse dump for inert waste. Instead, in accordance with Slovenian legislation, it has to be deposited on waste bump for non hazardous waste. Concentrations of all other metals are low and pose no problems for final disposal. Additional to slag analyses there has to be made a leaching test to determine the convenient type of landfill site. Conducted leaching test (Table 4) showed all concentrations under legislative values.

5 System "In-situ" in combination with three-stage flue gas treatment

It has to be emphasised that throughout the incineration the most efficient operation of "in-situ" system and flue gas treatment system was searched in order to find lowest emissions and at the same time to have the lowest quantity of remains and the lowest consumption of additives. Flue gas concentrations of SO_2 without lime addition were before flue gas treatment around 10g/Nm^3, what shows that almost all sulphur has "burnt out" and left primary chamber with flue gases.

The composition of the waste is presented in chapter 2 where detailed chemical analyses are presented. It can be seen, that the element that produces the highest quantity of pollutant emissions is sulphur, which is in the waste present as:

- pyrite (sulphide) – inorganic compounds of sulphur (for example: FeS_2) - inorganic acid,
- sulphur organic bound to C_nH_m molecules – organic acid,
- sulphate – sulphur is let loose only at very high temperatures,
- elementary sulphur.

Some sulphur can be found in ash after incineration. Common conversion of sulphur and sulphur compounds into gas is 95 percent. Only sulphur bound as sulphate does not converse. Waste containing free sulphur acid can cause the formation of SO_3 when incinerating.

Pilot incinerator has three stage flue gas treatment system with following order:

- semi-dry adsorbtion,
- bag filter and
- coke adsorber.

<u>Semi-dry adsorbtion</u> employs calcium hydroxide – slaked lime – ($Ca(OH)_2$ + water). It is sprayed into reactor in direction of flue gas stream. Lye lime solution reacts and neutralises acid components in flue gases. Neutralisation process forms salts and water. This process mostly removed sulphur oxide and some halogens.

The process of sulphur dioxide elimination with calcium hydroxide performs best at temperatures between 200 and 250 °C according to th e next reaction:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_4 + H_2O$$

Above mentioned characteristics of calcium hydroxide qualifies it as the most applicable for adsorbers.

<u>Bag filter</u> removes particles in flue gases, formed either in furnace or product of semi-dry adsorbtion. Bag filter clean up is solved with compressed air.

<u>Coke</u> is produced from coal and serves as third stage of flue gas treatment. It covers the whole cross-section of reactor so flue gases have to flow through. Coke adsorber is the final polish stage of flue gas treatment and removes the remaining acid components, heavy metals, hydrocarbon compounds, particles and dioxins and furans.

Acid emissions removal with "in-situ" system is supply of calcium oxide or lime directly into the furnace (primary chamber) what in case of acid sludge incineration ensures "in-situ" elimination of sulphur. Slaked or unslaked lime reacts with sulphur in furnace that is present in acid acid sludge in high quantities. With this system the sulphur is transformed into calcium sulphate in furnace at the time of combustion. The concentration of sulphur in untreated flue gases decreases up to five times. This system enables easier work of flue gas treatment devices to finish their work more efficient.

Use of lime ($CaCO_3$) – calcium carbonate – can be presented with next reactions:

$$CaCO_3 \rightarrow CaO + CO_2 \text{ – calcination}$$

$$CaO + SO_2 \rightarrow CaSO_3$$

$$\left.\begin{array}{l} CaSO_3 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 \\ CaO + SO_3 \rightarrow CaSO_4 \end{array}\right\} \text{calcium sulphate (gypsum)}$$

In the process of calcination the concentration of CO_2 in combustion chamber is raised and this is bad for combustion. Optimal temperature range for above mentioned reactions is between 800 and 850 °C. The a mount of lime needed depends on the mol relationship of Ca/S. Also, of big influence is the type of lime (softer is better).

If calcium oxide (CaO) is admixed into combustion chamber then the next reaction occurs:

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4$$

The reaction represents the way the concentration of SO_2 was lowered in combustion chamber during test acid sludge incineration from 10 g/m^3 to 3 g/m^3. The amount of gypsum ($CaSO_4$) produced can be arithmetically presented with the equation:

$$1 \text{ mol } SO_2 \rightarrow 1 \text{ mol } CaSO_4$$

$$m_{CaSO_4} = 2{,}125 \cdot m_{SO_2}$$

We can set next relationship of acid sludge incineration: 1 kg acid sludge → 12 m^3 flue gases, that is computed from next relationship of measured parameters:

- average gas emission of SO_2 in untreated flue gases is 10 g/m^3,
- one kilogram of acid sludge has around 60 g of sulphur (see analyses – Table 1).

Incineration of one kilogram of acid sludge produces according to below presented equation from 60 gram of sulphur 120 gram of sulphur dioxide:

$$S + O_2 \rightarrow SO_2$$

This all together gives 12 m^3 of flue gases per 1 kilogram of acid sludge.

Lowering the concentration of SO_2 from 10 to 3 g/m^3, stechiometrically produces according to above mentioned equation 178 g of $CaSO_4$ per kilogram of acid sludge. Also taking into account the efficiency of around 75 % the final amount of gypsum is approximately 240 gram. Adding this to around 100 gram of ash per kilogram of gudron, the total remains after incineration in combustion chamber with this system are between 30 to 35% of gudron quantity.

The system of admix of unslaked lime or lime into combustion chamber has negative impact on the process of combustion in primary chamber since it covers the burning layer of acid gudron and prevents air delivery from upper side to acid sludge and reactions of combustion on surface. Thus more supporting fuel has to be added to ensure appropriate temperature for semi – pyrolitic gasification in primary chamber. The temperature in primary chamber is very important for the ''in-situ'' system. If it exceeds 1000 °C the reaction of SO_2 removal turns around and calcium sulphate starts to decompose:

$$2\, CaSO_4 \rightarrow 2\, CaO + 2\, SO_2 + O_2$$

The quality and quantity of additive has big influence on the quality of sulphur removal from flue gases with this type of additive admix into primary combustion chamber. It has been determined during the test incineration that excellent and even distribution of appropriate quantity additive in entire combustion chamber is needed to lower considerably the concentrations of sulphur in flue gases. Too low amount of additive or bad distribution do not produce wanted result of lowering the concentration of sulphur in flue gases, while exceeded amount of additive "extinguishes" gudnon combustion thus produces material loss (needs to be bought) and unnecessary bigger amount of remains after incineration.

Figure 7 shows a simple device, made for admix of additive into primary combustion chamber of pilot incinerator. It was specially produced exclusively for acid sludge test incineration. Quantity of admixed unslaked lime is regulated with sequence regulator which is over software connected to other primary combustion chamber process parameters. During tests many different protocols of unslaked lime admix were performed.

6 Conclusion

Appropriate planning of all test trials with correct selection of incineration technology and technology of flue gas treatment together with precise execution of tests reveal, show that it is possible to incinerate acid sludge with very well and most promising results. It is also very welcoming that the concentration of SO_2 was able to get under the legislative value. Concentrations of heavy metals in slag show that only minor part has left the primary incineration chamber thus easing the work of flue gas treatment devices.

Reviews of all results have proven that the incineration technology is applicable for acid sludge treatment. Measured air emissions that were over legislative values can be lowered under regulation values with additional minor effort. Slag chemical analyses and leaching test demonstrate that there are some heavy metals in very high concentration thus not allowing slag disposal at inert waste landfill site where land filling is the cheapest.

Incineration of acid sludge is remedial that can be carried out in accordance with current local and EU regulations presently in force and represents the final and lasting solution with minimal influence on environment while processing.

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ključne riječi:	key words:
665.664.23 gudron, kiseli ostatak obrade sumpornom kiselinom	acid sludge
628.492 spalionica otpada	waste incineration plant
.004.64 gledište rizika za okoliš	viewpoint of environmental hazards
504.062.4 obnova ugroženih prirodnih resursa	restitution of threatened natural resources

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Primljeno / Received:

01.12.2002.