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Effect of Classical Eberhart Lime Kiln Modifications on Capacity and Lime Quality of Kilns

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While there are various factors affecting lime quality, the quality of raw material, calcination temperature and calcination time as well as the fuel type used are among most important factors. Some modernization activities were performed in classical Eberhart type lime kilns of a facility that is located in the city of Adana, Turkey. In this context, alterations were done in kiln heights of this facility and both new stack system and stack gas treatment units were mounted in the facility and in this way, polycyclic aromatic hydrocarbons (PAHs) having carcinogenic effect were anulled by keeping them at 900 ºC for at least 0.3 s. Loading raw materials and fuel into kilns through an automated system and similarly, loading unburned lime from kiln base to unburned lime bunker automatically have provided considerable advantages. The used kiln limestone was investigated in detail both under laboratory conditions and kiln regime calcination conditions and the factors affecting lime quality were determined through plenty of surface area, porosity measurements and chemical analysis. It was observed that, depending on the limestone content, dissolution accelerates after 850 ºC and when 900 ºC is reached for pure limestone in kiln applications, it is understood that the calcination is completed. Some of porosities which are opened in sections exposed to calcination for a long time in higher temperatures are blocked. In applications where it was understood that MgO and other impurities within the limestone are effective on the quality, it was seen calcination process was completed at low temperatures for limestone having more than 5 % MgO content. Due to aforementioned alterations performed on 8 modernized Eberhart type kilns of partner facility of this project, Nur Kirec Ltd. Sti., the facility now in a position to obtain emission license. In addition, capacity of this facility increased by 20 % active CaO ratios in produced quick lime has reached up to an average value of 92.

Key Words: Lime (CaO), Quality, Calcination, Limestone, Eberhart.

INTRODUCTION

The utilization of lime, which has been used as construction ingredient since the archaic ages as stated in 'De Architectura' book of Marcus Pollo (B.C. 27 - A.C. 14)[1], becomes prevalent today in chemistry and iron-steel production. It is almost certain

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that the lime will be used increasingly by many more sectors in the upcoming first 20 years. The most important reasons for this conclusion is that the limestone which is the raw material of the lime is very cheap and it is possible to produce lime under both primitive and developed technology conditions. In today's conditions, it is somehow possible to produce lime from 10 to 15 types of different carbonatic rock that contains more than 90 % $CaCO_3$ in their composition. However, the energy, that is the types of fuel, to calcinate this raw material in industrial scale is limited. These fuels are coal from fossil fuels, petroleum based fules (including LPG and natural gas) and petroleum coke that is among the final products in petroleum refineries[2-6].

Turkey is among the leading countries in Europe in terms of availability of cement and lime raw materials. Existence of limestone sources almost in every region of the country is another advantage for Turkey. It is seen that lime is produced in every region of Anatolia with solid fuels such as bushes, wood and coals in various kilns since the early ages. The kilns, in chronological order, are hillside type kilns, Classical Eberhart type kilns, Hungarian type kilns and Maerz type kilns. As seen in most of the European countries, all of these kilns are vertical shaft kilns. Hillside type bush kilns are no more used. Maerz type kilns become widespread while Hungarian type and Eberhart type kilns have gone through a lot of changes. Eberhart type kilns exist today in most cities of Anatolia and used for producing lime since 1950's. 90 % of lime produced by this type of kilns is offered for domestic market and petroleum coke has been utilized since 1986 as fuel in Eberhart type kilns. Petroleum cokes has become indispensable due to its various advantages compared to other solid fuels and because of its increase of lime quality with very low ash value by making a positive effect on calcination process. However, since petroleum coke includes carcinogenic polycyclic aromatic hydrocarbon (PAH) and since they create risk during their discharge to atmosphere through stack gases in kilns where there is no complete burning (< 900 ºC), a limitation was imposed its use by the Ministry of Environment since 1996. It was expressed there are harmful effects from petroleum coke if it is discharged to atmosphere through stack from kilns without keeping them above 900 ºC for at least 0.3 s after pulverizing in cement factories and Maerz type kilns and it was decided by the Ministry of Environment not to burn them in these types of kilns[7-9].

In this study, the possible effects of the modifications performed on both kilns and stack systems of a firm that has 8 Eberhart type kilns and that is situated in the city of Adana, Turkey, on lime capacity and quality which will be produced utilizing petroleum coke as well as the results on stack gas emissions were investigated.

Limestone and lime production: Limestone is a type of rock existing in nature in large amounts and it is not easy to have pure limestone under natural conditions due to existence of various elements within it. Theoretically, if the minerals other than carbonate in its composition are less then 1 %, 0.56 kg quick lime is obtained from 1 kg limestone. This amount is equivalent to 0.74 kg dead lime. Calcination of limestone is highly endothermic (heat receiving) operation and $CaCO_{3(s)}$ + heat → $CaO(s) + CO_{2(g)}$ requires 1792 kJ/kg amount of limestone energy consumption[2,3,10].

Dissolution temperature of limestone is about 1173 K_o (900 ºC) and 3029 kJ of energy is needed to obtain 1 kg of CaO after dissolution[11]. Calcination period is usually related with the piece dimension of limestone and it is accepted that small pieces are dissolved faster due to faster calcination and transformed to CaO by loosing CO_2. There are a lot of studies performed in the laboratory scale about this subject[12-14]. Borgwardt[12] determined in his studies performed in a reactor of fluidized bed that 0.25 s was necessary at 1000 ºC for calcination of 90 % of limestone pieces having a dimension of 10 μm while those having a dimension of 6 μm needed 40 s calcination time at 710 ºC for having the same calcination ratio. Differences were also seen in surface areas and porosities created in quick lime under these different temperatures and particle dimensions[10,12,15].

Although control of calcination conditions and limestone used in laboratory studies as raw material can be determined definitely, this can not be accomplished completely in lime kilns used by industry. Since the works in this study were performed in industry scale on 8 Eberhart type kilns of firm which has been producing lime since 1950s, it is impossible to give calcination temperature and calcination time even in minute scale. Therefore, the implemented calcination conditions will be given in the global scale. General characteristics of Eberhart type kilns that are used widely in Turkey for lime production are given in Fig. 1[16,17].

Almost all of the kilns that produce lime in Europe and Turkey have vertical shaft while horizontal shaft kilns are preferred in some developed countries, especially in USA. The kilns that are used for producing lime in Turkey have pre-heating, calcination and cooling sections and they have circular, elliptical, rectangular and ring-shaped cross-sections. Lime production is performed in kilns having dimensions between 15 and 25 meters by using solid, liquid and gaseous fuels. As of today, the quality of lime produced in Turkey in a year changes based on various parameters. These parameters are mainly the following: (a) Quality of limestone used for production (crystal structure, impurities, fragility), (b) Dimensions of limestone loaded into kiln, (c) Calcination speed (sudden heat, gradual heat), (d) Calcination temperature, (e) Calcination time, (f) Chemical reactivity, (g) Contraction characteristics (density, porosity), (h) Surface area, (i) Type of fuel used and its quality, and (j) Re-carbonation possibility[12].

The best known lime kiln having vertical shaft and parallel flow is Maerz type of lime kilns and these kilns have 2 or 3 kiln bodies that are parallel to each other. While fuel is fed for certain amount of time (15 min) for a kiln, the other kiln remains standby. Burning gases circulate around the standby kiln body and preheats the limestone within it. When the fuel feeding time is completed for the kiln in use, the fuel is fed to the standby kiln and in this way, calcination continues in alternation. There is a considerable amount of fuel savings in these types of kilns and energy consumption is about 850-950 kcal/kg quick lime.

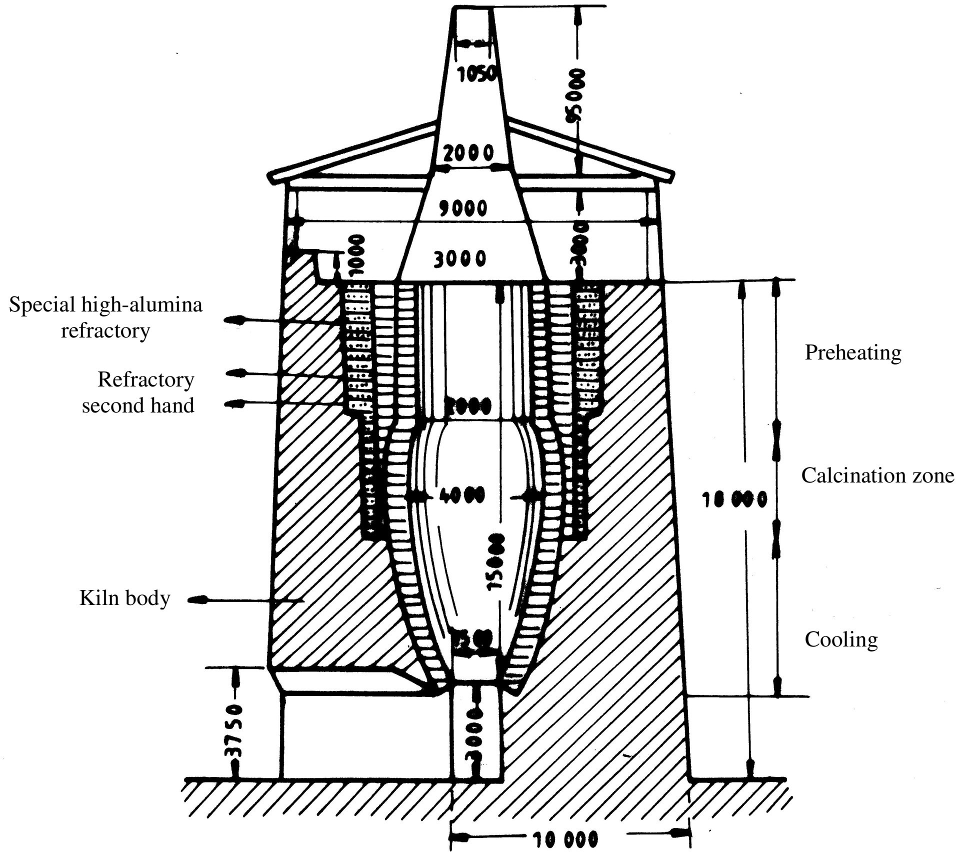


Fig. 1. Classical Eberhart type lime kiln (dimensions are in mm)

There are limited numbers of Maerz type kilns in Turkey while there are about 200 Eberhart type lime kilns in various cities of Anatolia which have been in use since 1950s. These kilns are vertical shaft type and they use solid fuels (coal). Limestone + coal is charged into kilns from top and the burning gases that came out of so called pit which is the main burning chamber preheat the incoming limestone + coal mixture and then discharged to atmosphere. The limestone that becomes subject to calcination completely in a temperature above 900 ºC moves towards to the bottom of the kiln as CaO and gets cooled slowly and then removed from the bottom of the kiln within 3 to 6 h intervals and in this way a continuous flow of the kiln becomes possible.

It does not matter which type of kiln is used for its production, the quality and usage purpose of the lime that is offered for market are important. Construction sector, iron-steel industry, sectors that use it as disinfectant and chemical industry all use lime with different characteristics. Therefore, it is possible that a lime that has ideal characteristics for one sector might be insufficient for some other sector.

In a calcination process, 44 % of $CaCO_3$ (100 %) must be removed from CaO as CO_2. This ideal condition can not be fulfilled in an industrial type lime kiln due to various reasons. Both foreign elements and minerals within the limestone that is used as raw material and sudden changes in the calcination regime prevent the occurrence of the transformation that must theoretically take place. It is known that dimension of limestone that is charged to the kiln affects the calcination time and while small size particles that start calcination at the same temperature complete their transformation earlier than the large size particles. Some of porosities that are formed due to CO_2 loss as a result of being subject to high temperature are closed back to due to extreme temperature. Therefore, it is obvious that the situations in the laboratory conditions where each parameter can be easily controlled and industrial type kiln conditions where these parameters can not be controlled are different.

EXPERIMENTAL

The raw materials used were taken from Ceyhan region limestone areas in Adana, Turkey. During sampling, rock types having no bedding planes were selected to eliminate any anisotropic effects in the measurements of the samples. Limestones present macroscopically different characteristics. It is light-coloured 'dirty white' with hardly any distinguished crystals; whereas, Microcracks were not present throughout the mass of limestones.

Analytical methods and techniques: Analyses were performed on limestone and lime samples by using the following analytical procedure.

(a) XRF (Siemens SRS 300 X-ray flouresans spectrometer) was used to determine the chemical compositions of limestone samples. (b) Transmitted light microscopy (Olympus BH-2) was carried out on polished thin sections of the limestone in order to identify the texture, shape and size of the grains. (c) Adsorption of nitrogen was performed on lime in order to evaluate the value of specific surface area by physical sorption isotherm data according to the method of Brunauer-Emmet Teller (BET). (d) Scanning electron microscopy (SEM) (Jeol 840 AJXA) was carried out on limestone and limes.

RESULTS AND DISCUSSION

Mineralogical and chemical characteristics in Nur lime kilns: The limestone field where the limestone used as raw material in modified lime kilns is licensed for the company and limestone is produced in limestone mine that is 500 m far from the kilns. The limestone that is produced with open facility method does not show completely homogeneous properties and there are some differences in its both chemical composition and mineralogical structure. The rocks fed to the kilns are analyzed and 3 main rock types are specified. These are pure limestone ($CaCO_3$ > 95 %), dolomite type limestone (MgO ratios are between 5 and 21 %) and clay and marl type limestone (50-53 CaO %). Micro-cracks observed in limestone having micritic structure are completely filled with sparicalcit crystals and dolomite crystals increase as one moves to dolomite type limestone. Detritic quartz and sequential opaque minerals (mostly limonite) are observed. In the limestone mine, thin layered and sequential clay bands are observed locally. Rarely seen fossil tracks are completely carbonized and took calcite filling form. MgO content of this clay and sand including limestone in which sometimes stilolytes are observed is quite low. Chemical contents of limestone that is burned in the kilns are given in Table-1.

TABLE-1
CHEMICAL CONTENTS OF LIMESTONE USED AS KILN ROCK BY NUR LIME COMPANY

Sample No.	CaO (%)	MgO (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Comments
201	55.43	0.41	0.03	0.09	0.03	Pure limestone, grey colour
202	55.36	0.42	0.04	0.14	0.05	Pure limestone, grey colour
203	54.89	0.42	0.07	0.70	0.11	Pure limestone, grey colour, with veins
204	54.66	0.46	0.68	0.26	0.17	Close to pure, but silica and iron are relatively high
205	54.88	0.42	0.15	0.47	0.13	Pure limestone, grey colour, with porosity
206	54.39	0.43	0.29	0.91	0.11	Pure limestone, blackish, with jeod
207	55.27	0.41	0.07	0.22	0.15	Pure limestone, grey colour, with jeod
208	35.23	17.50	0.05	0.18	0.08	Dolomite type limestone, dark grey
209	55.47	0.22	0.02	0.08	0.03	Aragonite, light honey colour
210	36.15	15.43	0.18	0.36	0.05	Dolomite type limestone, dark grey
211	53.01	1.20	0.15	0.29	0.17	Limestone with clay, marl, light brown
212	48.12	6.03	0.07	0.12	0.11	Dolomite type limestone

Modifications performed in classical eberhart type kilns of nur lime company: Nur Lime Company which produces lime with classical Eberhart type kilns since 1970s renewed all of its 8 kilns. The main bodies of these kilns are disassembled and their length was increased by 3 to 3.5 meter in order to make them compatible with the new stack system (Fig. 2).

The most important matter in this modification is that opposite flow situation in the classical kiln (limestone + coal was moving opposite to the gas discharge) was eliminated by new heat-resistant new stack pipe that was brought down to 3.5-4.0 meter below the top of kiln and all of gas discharge passes through stack pipe. In this way, the limestone + coal mixture that flows down from top of the kiln moves down by getting heated slowly and becomes quick lime by complete calcination above 900 ºC in the pit region. Carbon dioxide and burning gases that come out during this time move up through heat-resistant stack that is suspended from top in the middle of the kiln and reach to purification unit and then are discharged to atmosphere.

The temperature of the exhaust gases that are recorded to observe the effect of these changes are measured by a thermocouple that is mounted below about 40 cm of the top section of the kiln. Limestone + coal feeding is accomplished through a simplified, automated conveyor belt system.

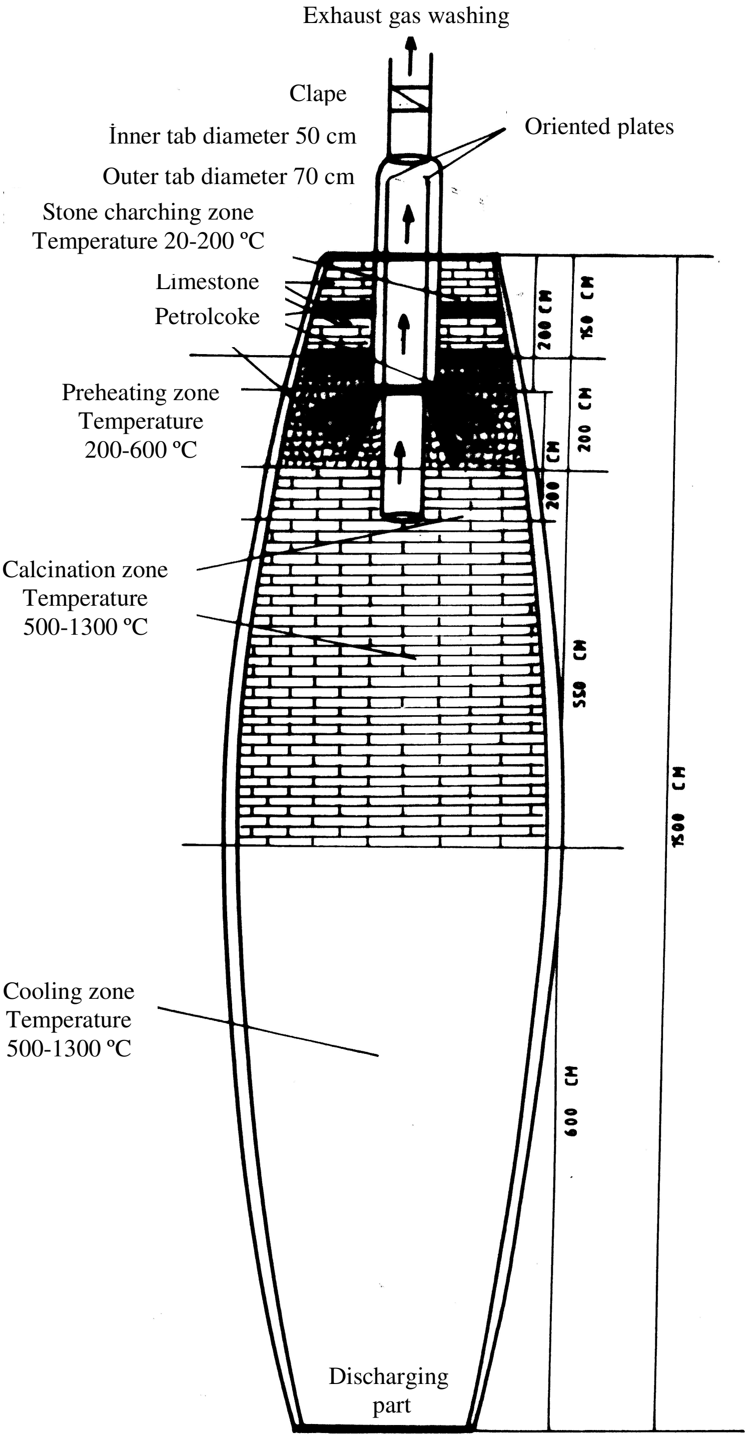


Fig. 2. Modified Eberhart type lime kiln

The modifications performed on classical Eberhart type kilns were not limited by kilns only and modifications were also anticipated on stack systems. The washing unit called wet filter system is shown in detail in Fig. 3. Since petroleum coke is burned in the kilns and since up to 5 % sulphur is discharged directly to atmosphere as SO_2, serious air pollution results; therefore, exhaust gases are washed with CaO or NaOH (caustic) pulp and sulfur dioxide emissions are taken under the limit values due to $CaSO_4$ formation. The particulate matter (PM) concentrations in stack gases are also reduced in a considerable amount with the washing unit.

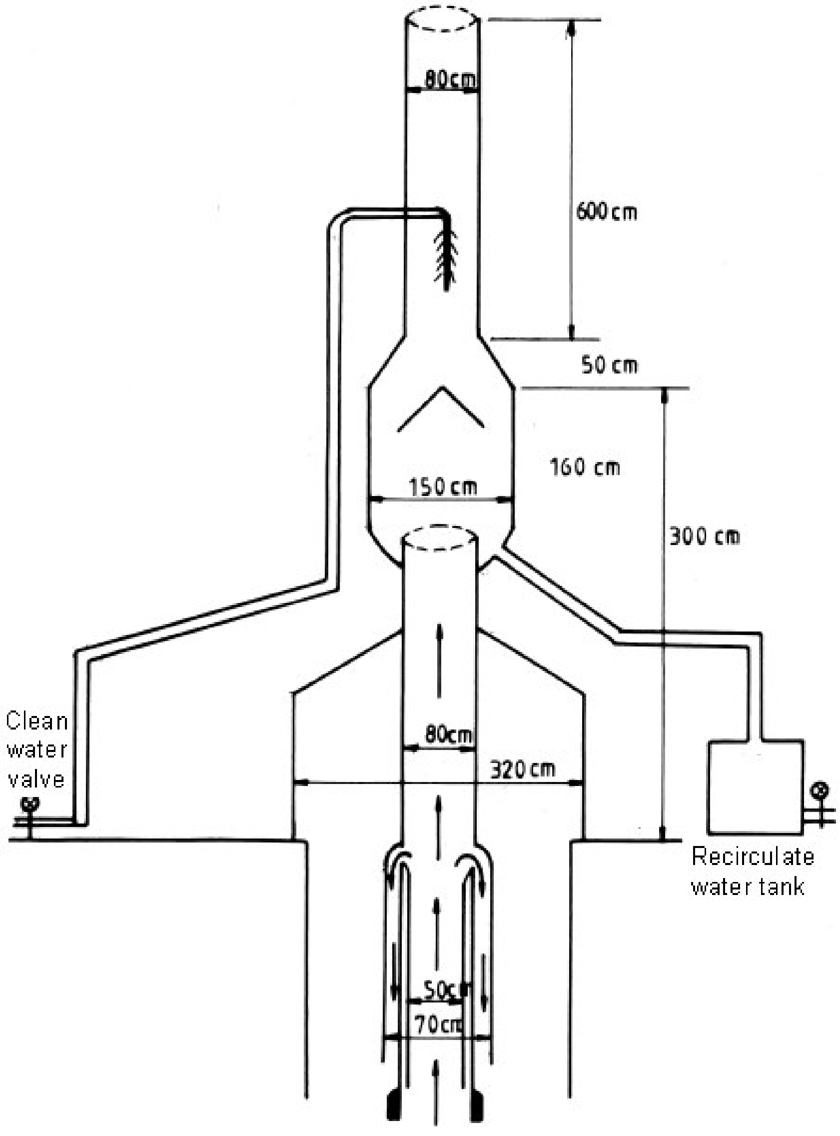


Fig. 3. Modifications made in kiln stacks and schematic view of the purification unit

Emission measurements in modified kiln stacks: In this study, a lot of exhaust gas emission measurements are performed in modified kiln stacks and modified bodies of kilns of study partner Nur Lime Company facilities that are established in Cokcapinar (Ceyhan-Adana) in order to determine whether or not emission values foreseen by RCAPCIF (Regulation for Control of Air Pollution Caused by Industrial Facilities) are complied with. Air polluting parameters in exhaust gases that are discharged to atmosphere after passing through kilns stacks and treatment units are recorded systematically and mass flow rates of polluting parameters *i.e.*, CO, SO_2, NO_x and P.M. are determined. The resulting averages of measured values are given for each kiln in Table-2.

Since the petroleum coke burned in the kiln in 0-20 mm dimensions has carcinogenic characteristics, PAH (polycyclic aromatic hydrocarbon) measurements were also performed. Analysis of petroleum coke that is loaded on top of kilns together with limestone with a semi-automatic system without pulverizing is given in Table-3. Although this fuel has high caloric value (7674 kcal/kg original lower limit), its sulfur content reached up to 5 % and this creates a danger in terms of air pollution. However, while average value of sulfur decreases since some of it is transformed into lime during calcination, the burning sulfur causes $CaSO_4$ formation while passing through the stack and in this way, sulphur emissions are automatically reduced. The measurements performed on the last point before it is discharged to atmosphere, SO_2 readings show that all values measured when the treatment system is working are below the limiting values foreseen by RCAPCIF. When the treatment system was shut off for the testing purposes, SO_2 values measured were above 2000 mg/m^3. In addition, it was seen that CO emissions for most of the measurements were above the limit values and they sometimes reach up to 2500 ppm values. This situation was observed when there was no full burning in the kiln due to inadequate amount of air and when the fan on the base of the kiln can not provide enough amount of O_2 that will facilitate adequate burning to the pit region. It was also seen that when the full burning available, with the help of treatment system, exhaust gas emissions are always below the limiting values.

Since only a couple of institutions in Turkey can perform PAH (polycyclic aromatic hydrocarbon) measurements, these measurements were conducted by TUBITAK (MAM) Chemistry and Environment Institution personnel (Table-4).

ISO 11338-1, 2 Standard Method was used for measurements and sampling. As can be seen in values given in Table-4, when the washing system was on and when the kilns were working in full capacity, mass flow rate values of carcinogenic PAH emanating from petroleum coke were found to be under the limit values. This result shows that the petroleum coke that provides a temperature above 900 ºC during calcination of limestone and all exhaust gases are cooled as they pass through the stack, that is made of heat resistance cast material and that is situated right above the calcination region which is also called pit, before passing through gas treatment unit.

TABLE-2
STACK GAS EMISSION VALUES FOR 8 MODIFIED EBERHART TYPE LIME KILNS OF NUR LIME COMPANY WHEN THEY ARE WORKING IN FULL CAPACITY

Parameters	Kiln No. 1	Kiln No. 2	Kiln No. 3	Kiln No. 4	Kiln No. 5	Kiln No. 6	Kiln No. 7	Kiln No. 8
Measurement date	24.05.2007	24.05.2007	14.06.2007	14.06.2007	19.07.2007	23.08.2007	23.11.2007	23.11.2007
Fuel type	Petroleum Coke	Petroleum Coke	Petroleum Coke	Petroleum Coke	Petroleum Coke	Petroleum Coke	Petroleum Coke	Petroleum Coke
Heating power	9.59 MW	9.59 MW	9.59 MW	9.59 MW	9.59 MW	9.59 MW	9.59 MW	9.59 MW
Fuel amount	1100 kg/h	1100 kg/h	1100 kg/h	1100 kg/h	1100 kg/h	1100 kg/h	1100 kg/h	1100 kg/h
Kiln efficiency	% 65	% 68	% 77.4	%77	%68	%75.4	%92.7	%84.5
Stack dimension	1 m	1 m	1 m	1 m	1 m	1 m	1 m	1 m
Stack height	26 m	26 m	26 m	26 m	26 m	26 m	26 m	26 m
Exhaust gas treatment system	Wet filter	Wet filter	Wet filter	Wet filter	Wet filter	Wet filter	Wet filter	Wet filter
Gas temperature (°C)	191.00	197.00	205.66	400.00	156.00	224.00	153.66	190.00
O_2 (%)	12.06	12.03	12.29	12.37	7.80	14.83	7.80	13.10
Stack gas speed	5.66	6.10	5.70	5.20	5.26	5.90	6.20	5.3
Stack gas volume flow rate (m^3/h)	15 995.16	19 215	17 995	16 380	16 569	19 585	19 530	16 695
Smoke	2	2	2	1	2	2	2	2
Dust (P.M.) (mg/Nm^3)	54.00	47.33	60.66	47.66	52.66	65.66	57.66	47.00
CO (mg/Nm^3)	176.33	168.33	171.00	850.00	176.33	442.00	174.66	440.66
SO_2 (mg/Nm^3)	26.33	87.33	108.00	144.33	40.66	38.33	41.00	84.33
NO_x (mg/Nm^3)	67.00	80.66	73.33	83.66	24.00	21.00	23.00	2.00
				Mass flow rates (Kg/h)				
Dust	0.468	0.395	0.489	0.485	0.351	0.575	0.423	0.483
SO_2	0.786	0.730	0.870	1.468	0.255	0.335	0.301	0.867
CO	1.298	1.407	1.379	8.647	1.110	3.868	1.284	4.532
NO_X	0.496	0.675	0.591	0.851	0.151	0.183	0.169	0.021
Comments	All parameters are under limit values	All parameters are under limit values	All parameters are under limit values	CO emission is a little high	All parameters are under limit values	CO emission is a little high	All parameters are under limit values	CO emission is a little high

TABLE-3
ANALYSIS RESULTS OF PETROLEUM COKE THAT IS USED AS FUEL IN MODIFIED LIME KILNS BY NUR LIME COMPANY

Analysis	Dry air	Dry	MAF value without ash and humidity	Original value as received	Test method
Total moisture (%)	-	-	-	6.81	ISO 579
Inherent moisture (%)	0.48	-	-	-	ASTM D 3173
Ash (%)	0.77	0.77	-	0.72	ISO 1171
Volatile matter (%)	11.55	11.61	11.70	10.82	ISO 562
Higher calorie value (Cal/g)	8423	8464	8530	7888	ISO 1928
Lower calorie value (Cal/g)	-	8275	8339	7674	ISO 1928
Total sulfur (%)	4.34	4.36	-	4.06	ISO 351
Origin of petroleum coke venezuela	Analysis are performed by Standard Laboratories Ltd.				

In order to verify that the temperature here is above 900 ºC, continuous temperature measurements were conducted by TUBITAK (MAM) personnel on the stacks (Fig. 4) of modified Eberhart type lime kilns of Nur Lime Company and it was seen that all exhaust gases enter to kiln stack above 900 ºC, the gases stay there for at least 0.3 s and after PAHs are ruptured, they go to gas treatment unit and then they are finally charged to atmosphere. Temperature measurement on 8 modified stack system and staying time of gases in the stack are shown all together in Table-5.

As can clearly be seen in Table-5, all lime kilns treated at least 0.3 s above 900 ºC temperature condition and in this way, the most important problem, that is discharging the exhaust gases to atmosphere after decomposing PAHs that originate from using petroleum coke as fuel, was solved. It is indeed verified that PAH measurement results (Table-4) all the carcinogenic matters that result from burning petroleum coke are discharged to atmosphere in concentration values that are under the critical limit values.

The following results are concluded when values limit observed by RCAPCIF (Regulation for Control of Air Pollution Caused by Industrial Facilities) are taken as basis, that was published in 2004 by the Ministry of Agriculture and Forestry, for air pollutants that are discharged during calcination of limestone whose petrographic and chemical characteristics are given in Table-1 where petroleum coke is used as fuel in classical Eberhart type kilns that are modified and whose stack system is changed:

According to the E-5.C of RCAPCIF, particulate matter (dust) emissions within the exhaust gases that are discharged to atmosphere from stack when solid, liquid or gas fuels are used in lime kilns must not exceed 200 mg/Nm^3 value. The measurements that were performed several times for 8 stack kilns show that there were no values above 200 mg/Nm^3 value when the gas treatment system is working. However, when the gas treatment system was off, it was seen that the above mentioned limiting values were exceeded.

TABLE -4
POLYCYCLIC AROMATIC HYDROCARBONS (PAH) MEASUREMENT RESULTS IN MODIFIED LIME KILN STACKS

PAH member	Concentration (μg/m^3)								Mass flow rate (g/h)	
	Kiln stack number 7				Kiln stack number 8					
14.06.2007	1st measure	2nd measure	3rd measure	Mean value	1st measure	2nd measure	3rd measure	Mean value	Number 7	Number 8
Naphthalene	<0.01	0.58	<0.02	0.20	1.69	1.25	11.69	4.88	0.001	0.020
Acenaphtalene	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.02	<0.01		-
Acenaphthene	<0.01	8.28	3.82	4.04	<0.01	10.15	128.43	46.19	0.014	0.194
Fluorine	1.58	2.25	1.35	1.73	1.80	0.99	9.36	4.05	0.006	0.017
Phenanthrene	5.14	6.16	4.23	5.18	12.04	15.92	26.95	18.30	0.018	0.077
Anthracene	1.24	1.17	<0.02	0.81	1.53	0.71	13.45	5.23	0.003	0.022
Fluoranthene	0.59	1.24	4.13	1.99	<0.01	0.16	<0.02	0.06	0.007	-
Pyrene	2.80	4.22	6.26	4.42	5.64	3.10	101.56	36.76	0.015	0.154
Benz(a)anthracene	0.27	0.23	0.70	0.40	0.54	1.08	3.25	1.62	0.001	0.007
Chrycene	0.26	0.22	0.53	0.34	0.28	2.30	10.45	4.34	0.001	0.018
Benzo(b)fluoranthene	0.66	0.56	0.23	0.49	1.44	<0.01	4.35	1.93	0.002	0.008
Benzo(k)fluoranthene	0.63	0.31	0.72	0.55	3.00	0.56	7.59	3.72	0.002	0.016
Benzo(a)pyrene	**0.49**	**<0.01**	**<0.02**	**0.17**	**<0.01**	**<0.01**	**7.84**	**2.62**	**0.001**	**0.011**
Dibenzo(a.h)anthracene	**<0.01**	**<0.01**	**<0.02**	**<0.01**	**<0.01**	**<0.01**	**<0.02**	**<0.01**	**-**	**-**
Benzo(g.h.i)perylene	<0.01	1.02	3.07	1.36	<0.01	<0.01	<0.02	<0.01	0.005	-
Indeno(1.2.3-c.d)pyrene	3.00	0.41	1.95	1.79	0.41	<0.02	<0.02	0.15	0.006	0.001

PAH member	Concentration (μg/m^3)								Mass flow rate (g/h)	
	Kiln stack number 1			Gas flow rate (Nm^2/h) 2668 Average	Kiln stack number 4			Gas flow rate (Nm^2/h) 3367 Average		
4.12.2007	1st measure	2nd measure	3rd measure		1st measure	2nd measure	3rd measure		Number 1	Number 4
Naphtalene	0.033	0.08	0.128	0.080	0.781	0.212	1.017	0.670	0.0002	0.0022
Acenaphtalene	0.09	0.748	0.160	0.333	0.174	0.098	1.149	0.474	0.0002	0.0015
Acenaphtene	<0.11	<0.11	0.184	0.184	0.123	< 0.110	< 0.110	0.123	0.0004	0.0004
Fluorene	0.942	2.916	0.606	1.488	0.714	0.433	4.702	1.949	0.0039	0.0065
Phenanthrene	0.889	1.23	0.875	0.998	0.351	0.333	0.289	0.324	0.0026	0.0010
Anthracene	0.069	0.336	0.078	0.161	0.005	0.135	0.051	0.064	0.0004	0.0002
Fluoranthene	1.654	0.429	1.887	1.323	2.450	3.021	2.235	2.568	0.0035	0.0086
Pyrene	1.449	2.729	0.850	1.676	0.907	2.616	3.244	2.256	0.0044	0.0075
Benz(a)anthracene	<0.007	<0.007	<0.007	0.006	3.572	0.537	0.785	1.631	0	0.0054
Chrycene	0.329	0.541	0.568	0.479	0.670	4.220	1.007	1.966	0.0012	0.0066
Benzo(b)fluoranthene	<0.006	<0.006	0.01	0.010	3.572	0.537	0.785	1.631	0	0.0054
Benzo(k)fluoranthene	<0.009	1.500	0.031	0.765	1.469	2.002	2.619	2.030	0.002	0.0068
Benzo(a)pyrene	0.334	0.482	0.052	0.289	0.354	0.335	1.637	0.775	0.0007	0.0026
Dibenzo(a.h)anthracene	0.443	0.837	0.586	0.622	2.379	1.510	30.840	11.576	0.0016	0.0389
Benzo(g.h.i)perylene	<0.03	0.905	1.146	1.025	1.230	0.440	2.467	1.379	0.0027	0.0046
Indeno(1.2.3-c.d)pyrene	0.318	0.448	0.472	0.413	0.125	0.152	1.647	0.641	0.0011	0.0021

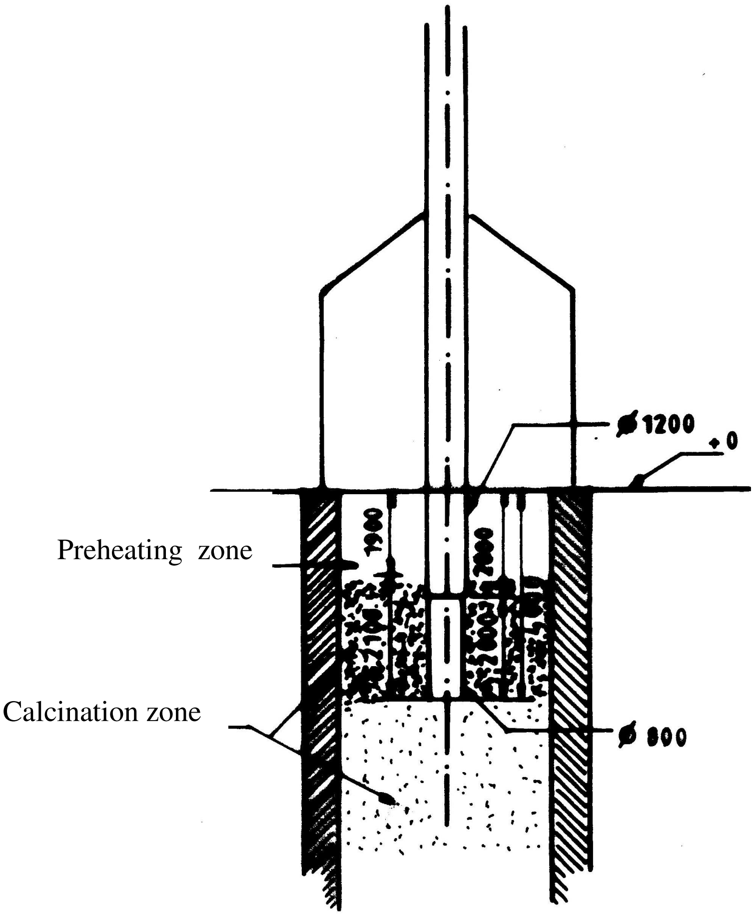


Fig. 4. Schematic view of modified Eberhart kilns where temperature and staying times are measured

Smoke ratio (Bacharach scale): According to the article[18] Annex-5.C.5.3.3 of the same regulation, smoke degree of the discharged gases from kiln stacks must not exceed 2. It was clearly observed at the end of measurements that smoke scale had never exceeded the value of 2 in any of the measurements.

CO: It is foreseen by RCAPCIF regulation that when petroleum coke is burned in a lime kiln, the fuel must stay for at least 0.3 s above 900 ºC in the region where the fuel is pulverized or loaded. Pulverization system does not exist in the modified classical Eberhart kilns.

Some weighed amount of petroleum coke is laid down so as to create a homogeneous level on top of the kiln with the help of a semi-automatic system. The petroleum coke + limestone that moves down as time goes by in parallel with the calcination speed starts releasing gas after 300 ºC. However, due to the structure of the stack, the exit direction of exhaust gases are not towards the top of the kiln but

TABLE-5
MINIMUM STAYING TIMES OF PETROLEUM COKE THAT IS LOADED TO MODIFIED KILN STACKS OF NUR LIME COMPANY IN 900 °C CALCINATION REGION

Stack No.	Stack diameter (m)	Gas speed (m/s)	Gas temp. (°C)	Stack area (m^2)	Gas flow rate (m^3/h)	Gas pressure mbar	Minimum staying time at 900 °C (s)	Minimum necessary stack height from beginning to 900 °C	Comments
1	0.8	5.200	615	0.5	9360	1001	2.70	0.24	Suitable
2	0.8	5.200	468	0.5	9360	1001	1.81	0.24	Suitable
3	0.8	4.740	606	0.5	8532	1001	2.56	0.21	Suitable
4	0.8	6.460	528	0.5	11628	1001	1.06	0.29	Suitable
5	0.8	5.070	531	0.5	9126	1001	1.19	0.23	Suitable
6	0.8	5.440	484	0.5	9800	1001	2.10	0.25	Suitable
7	0.8	5.375	588	0.5	9675	1001	0.81	0.24	Suitable
8	0.8	6.200	345	0.5	11160	1001	1.03	0.28	Suitable

These measurements were performed by TUBITAK MAM personnel upon the request of Nur Lime Company using heat resistant thermocouples and continuous sensors and staying times of fuel above 900 °C temperature. Necessary stack height in meters from the beginning of stack unit until the region where temperature reaches above 900 °C and volume of region that is subject to 900 °C temperature were calculated.

Calculation of void volume from the formula:

$$V = \left(D_1^2 - D_2^2\right)\frac{\pi h}{4}$$

$t = \frac{V_b}{Q_s}$ was used.

V = Volume of reactor region above 900 °C
V_b = Void volume in region of 900 °C
D_1 = Reactor diameter
D_2 = Stack diameter in 900 °C region
h = Height of 900 °C region
t = Staying time

towards heat resistant casting ring and therefore they are discharged from stack after being subject to a temperature above 900 °C and then pass through gas treatment unit. According to the RCAPCIF regulation, 200 mg/Nm^3 limit value in CO concentration is not a condition for lime kilns. However, the flow rate must not exceed 50 kg/h as stated in Annex-3.d.3. It was seen that CO emission in the lime kilns where measurements are performed exceeds 200 mg/Nm^3 value during the first charging but it does not exceed 50 kg/mass flow rate limit value.

SO_2: When volumetric oxygen amount is taken as 7 %, it is foreseen that SO_2 concentration emission in exhaust gases must not exceed 400 mg/Nm^3 and mass flow rate must not exceed 60 kg/h according to Annex-3.d.3. When 4.5 % sulfur containing petroleum coke is burned in the subject matter lime kilns, it is expected that SO_2 emission must be high. However, the measured values are below the limit values. The most important reason for this is that the sulfur is consumed in considerable amount during the chemical reaction of CaO that is used during gas treatment with water and stack gas (280-400 °C). On the other hand, some sulfur is also transformed to quick lime during calcination. CaO percents together with sulfur measurements were performed on quick lime samples and it was determined that it contains an average of 0.30 % sulfur in it.

NO_x: According to Annex-3-d of RCAPCIF regulation, nitrogen oxide emissions within exhaust gases in lime kilns must not exceed 20 kg/h value. The measured nitrogen oxide values were nowhere close to this limit values in any of the lime kilns and it was determined that mass flow rate values are around 1 kg/h.

These results show that there is no harm using petroleum coke as a fuel due to renovations performed in the gas treatment units of kiln stacks.

Lime quality: Chemical and mineralogical properties of limestone are the most important parameters affecting quality in lime production. Nur Lime Company that is the project partner in this study loosens Mesozoic age lime rocks having Olistrostrom characteristics that are in Bulgurkaya formation in Cokcapinar (Adana-Ceyhan) location which is called Alisan Hill with drilling-exploding method in the open facility and after they are classified in +40 -80 mm range in breaking-sieving facility. They are laid down in a way to form a homogeneous thickness from the top of the kiln with a semi-automatic mechanism. The results of chemical analysis of the limestone for both of those that is tested in the laboratory conditions and for those that is used in kilns by Nur Lime Company are given in Table-6.

TABLE-6
CHEMICAL CONTENTS OF LIMESTONE THAT IS USED AS TEST SAMPLES AND AS KILN ROCK

Sample No.	$CaO/CaCO_3$ (%)	$MgO/MgCO_3$ (%)	SiO_2 (%)	Fe_2O_3 (%)
NK1	54.30-96.91	1-38-2.90	0.10	0.24
NK2	55.18-98.48	0.40-0.84	0.16	0.21
NBK1	53.93-96.25	0.90-1.89	1.27	0.34
NBK2	52.53-93.76	0.99-2.08	2.76	0.82
NKD1	53.47-95.43	2.00-4.20	0.16	0.31
NKD2	52.94-94.00	2.37-4.98	0.40	0.37
NDK1	52.61-93.90	0.80-1.68	3.48	0.92
NDK2	53.59-95.65	0.40-0.84	2.87	0.87

Another important parameter that affects lime quality is the calcination temperature. Calcination starts after 600 ºC for dolomite type limestone while CO_2 gas exit accelerates after 700 ºC for pure limestone. Calcination is completed at 820-900 ºC temperature under normal conditions (eqn. 1):

$$CaCO_3 + ISI \rightarrow CaO + CO_2 \quad (1)$$

The amount of heat that is necessary for complete calcination of a limestone differs depending on the partial pressure of CO_2. Calcium carbonate decomposed completely at 898 ºC under 1 atmosphere pressure in 100 % CO_2 regime. Decomposition starts from wall and develops towards center. 150-350 ºC temperature difference can be seen in calcination temperatures for calcination that takes place in either in fluidized bed or horizontal shaft kilns and for calcination taking place in the laboratory conditions. Commadre *et al.*[10] analyzed the effect of temperature changes and calcination times on the lime quality for calcinations that are conducted using only atmospheric gas within the reactor under laboratory conditions (Table-7).

TABLE-7
CALCINATION PROCESS CONDUCTED UNDER LABORATORY CONDITIONS IN DIFFERENT TEMPERATURE AND TIMES [Ref. 10]

Atmosphere	Calcination temperature (ºC)	Time (s)	Calcination (%)	Specific surface area m^2/g lime
N_2	600	3600	10.11	–
N_2	600	5400	24.28	79.28
N_2	700	1860	50.09	–
N_2	700	1920	53.81	–
N_2	700	2520	73.04	46.66
N_2	750	1860	95.06	32.81
CO_2	900	2700	36.10	15.64
CO_2	910	1920	59.70	10.08
CO_2	920	1200	71.80	11.26

Partial pressure of CO_2 is important for transformation of limestone to CaO (quick lime) through calcination and it affects calcination temperature and time. Since the decomposition after heating in lime kilns is discharged to atmosphere together with CO_2 gases emanating from limestone, the effect of partial pressure CO_2 within the kiln is limited.

The subject matter limestone that is used in 8 modified kilns belonging to Nur Lime Company and whose chemical contents are given in Table-5 was exposed to calcination at 850, 900 and 950 ºC and surface area measurements were performed on the obtained quick lime. The results are shown comparatively in Table-8.

TABLE-8
SURFACE AREA MEASUREMENTS ON QUICK LIME THAT IS OBTAINED AFTER LEAVING IT FOR CALCINATION IN LABORATORY AT 850, 900 AND 950 ºC TEMPERATURES

Sample No.		NK1	NK1	NKD1	NKD2	NDK1	NDK2	NBK1	NBK2
Surface area before calcination (m^2/g) (full isotherm)	BET	0.61	0.91	1.18	0.91	0.85	1.41	3.93	2.19
	Langmuir	0.78	1.08	1.48	1.08	1.07	1.77	4.89	2.68
Total porosity before calcinations (mm^3/g)		1.04	1.58	2.45	1.58	1.36	2.15	5.93	3.92
850 ºC, Surface area after calcination (m^2/g) (single point)		3.633	3.143	3.591	3.927	2.655	2.772		
850 ºC, Surface area after calcination (m^2/g) (multiple points)	BET	3.99	4.34	3.99	4.41	2.96	3.05		
	Langmuir	5.09	3.45	5.09	5.57	3.75	3.94		
Comments		Porosity increased							
900 ºC, Surface area after calcination (m^2/g) (multiple points)	BET	6.72	5.22	7.04	7.31	5.01	5.19	5.58	4.44
	Langmuir	9.12	6.71	9.47	9.58	5.50	6.84	7.37	5.78
	Total porosity	12.48	8.87	12.12	12.51	7.77	9.39	7.921	7.49
Comments		Pores are opened very well.							
950 ºC, Surface area after calcination (m^2/g) (multiple points)	BET	5.12	5.16	7.74	9.63	6.70	6.82	5.72	3.88
	Langmuir	6.93	6.63	10.15	12.69	8.88	9.29	7.52	5.06
	Total porosity	8.37	8.24	13.07	16.45	9.83	12.03	8.50	5.84
Comments		Some of the pores are closed back.							

It was seen that at 850 ºC, the lime did not get white completely and $CaCO_3$ within the quick lime that could not exposed to calcination completely preserved most of its original state. The 900 ºC temperature is adequate for transformation of limestone to quick lime.

SEM analysis: Fifteen samples that are calcinated in modernized Eberhart type kilns and transformed to quick lime were sent to TUBITAK (MAM) for SEM analysis. It is well known that some observations can be done in terms of lime quality based on the SEM images. Under ideal conditions, it can be seen on SEM images of quick lime which is obtained after transformation of calcinated pure limestone formed after CO_2 leaves the rock are quite homogeneous and that their surface area measurements are in general large ratio wise. However, while unopened void structures are observed on quick lime obtained from limestone that could not heated well, SEM images of quick lime that is overheated show that some the cavities are closed back (**Plate-1**).

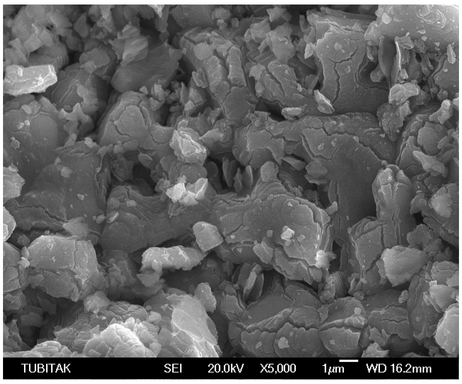
Measurement results for active CaO, MgO, SiO_2 and S samples of quick lime produced in modified Eberhart type lime kilns: After the limestone in dimensions of +40-80 mm produced as kiln rock in limestone mine is transformed into quick lime under kiln calcination conditions, active CaO, MgO, Al_2O_3, SiO_2 and S contents were determined on representative samples received from iron-steel producer firms such as Isdemir, Ekinciler and Yazici. The monthly averages from these analysis are given in Table-9.

TABLE-9
ACTIVE CaO, MgO, Al_2O_3, SiO_2 AND S CONTENTS ON QUICK LIME SAMPLES THAT ARE OBTAINED IN MODERNIZED EBERHART TYPE KILNS

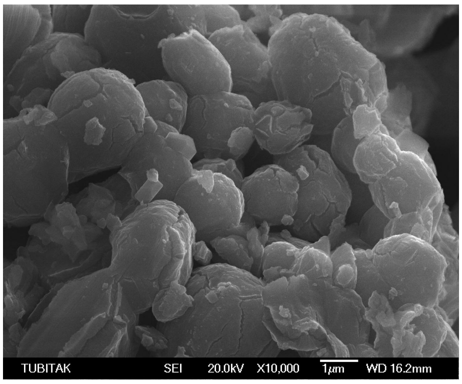
Total CaO (%)	Active CaO (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	Al_2O_3 + SiO_2 (%)	S	LOI	Impurity (%)	The firm sent by
	91.98	0.55	0.08	0.29	0.38	0.34	2.41	-	Isdemir
	93.22	-	-	-	-	-	2.44		Ekinciler
93.93	90.20	2.17					1.55	1.03	Yazici

LOI = Loss on ignition.

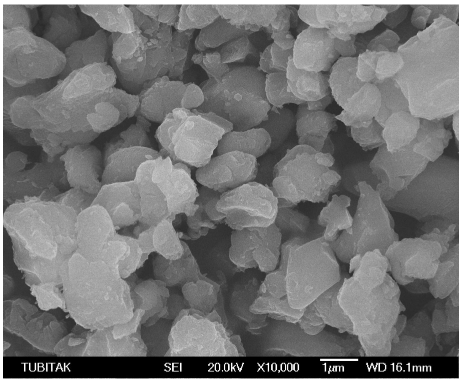
The request for part quick lime by iron-steel industry between Dortyol-Iskenderun region, primarily Isdemir, keeps increasing day by day. 35-40 % of quick lime produced daily in modernized Eberhart type kilns is shifted to these factories at the same day. The samples taken the same date systematically are analyzed in the chemistry laboratories of the related firms and evaluations for higher and lower limit values in terms of some parameters are performed. It is requested that active CaO must be above 85 %, Al_2O_3 + SiO_2 must be below 2 %, superheating loss must be below 4 % and S must be below 0.3 %. Although the quick lime that does not meet these requirements is accepted, a penalty procedure is implemented. When monthly average values given in Table-9 are analyzed, it can easily be seen that quick lime produced by modernized Eberhart type kilns can comfortably meet the limit values.



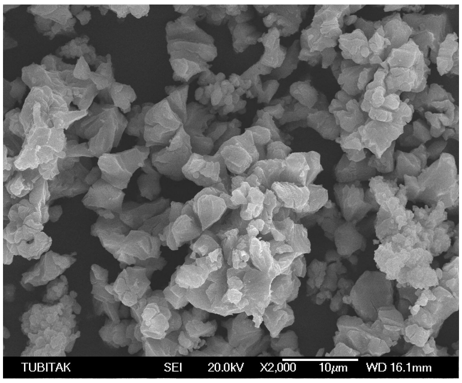
Homogeneous distributed lime having plenty of pores that is defined as good lime in the market.



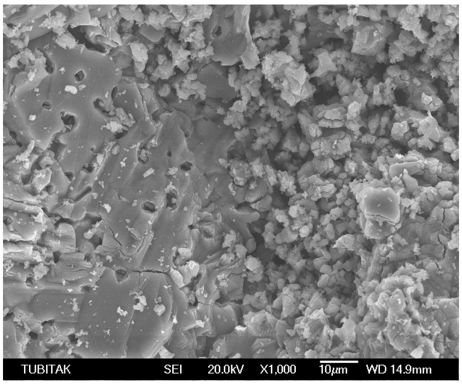
Another example for good lime. Pore amounts are in maximum level.



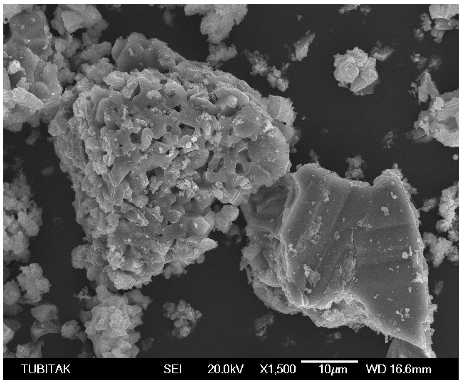
Good lime that is well calcinated and that have maximum amount of pores.



Another example for good lime. Non-porous sections can be seen rarely at some sections.



Taken from samples that are known as bad lime in the market. Possible reason for this is either overcooking or impurities within the limestone.



Closed or never opened pores. Bad lime.

Plate-1

Factors affecting lime quality and effect of modifications performed in kilns on lime quality: The limestone, whether it is used in classical or modernized Eberhart type lime kilns as raw material, is in dolomite type limestone, clay type and marl characteristics. Since it is produced with open mine operation method, there is no change in the quality of raw material. Since automation was accomplished with the modifications performed, a considerable amount of savings was accomplished in time and the amount of limestone to be loaded in kilns in one time was taken under control. Similarly, there is no change in the quality of petroleum coke that is used as fuel and it is possible to adjust the amount of petroleum coke to be charged in each party. Since loading is made into bunkers with loaders, the amount can be controlled by weight in kg basis with automatic weighing mechanism. The second important parameter on lime quality is calcination regime. The modifications made have created important changes in this regime. While the limestone in classical kilns reaches to calcination region that is accepted to be at 900 ºC on kiln top in about 3 to 4 h, the same road can be travelled in about 2 to 3 h in the modernized system. In addition, since the temperatures are read on an electronic medium, fan speeds can be adjusted and considering the remaining times in certain temperature, under- or over-heating can be controlled.

In the calcination process that is currently implemented in the 8 modernized lime kilns of Nur Lime Co., 9 tons of limestone and 800-900 kg petroleum coke are loaded in every 1 to 3 h to each kiln. While these raw materials that are loaded in pre-heating (initial calcination) stage move from top of the kiln down slowly, approximately after 2 times of discharging time (maximum 6 h), they reach to the real calcination region. Remaining time of each party in this region is maximum 3 h. When necessary, this time can be shortened up to 1.5 h by supplying extra air from the base fans. This method which is also called fast cooking is applied during peak demand periods since active CaO per cent especially in iron-steel industry is affected negatively due to overcooking. In fact, it is known from the results of a lot of experiments performed under laboratory conditions that the formula for the lime process is given as follows[10]:

$$\tau = \frac{m_i - m_f}{0.44 m_i} \tag{2}$$

where, τ denotes the calcination time, m_i is the initial mass of limestone and m_f shows the mass of limestone after calcination (975 ºC) (quick lime).

However, in an industry type of application, there are plenty other factors that affect this general process. Therefore, considerable deviations are observed in both calcination time and calcination temperature. Continuous recording and monitoring in an electronic environment to see whether adequate oxygen is provided to kilns during burning or not through protected, heat-resistant oxygen sensors are important innovations that are made in classical Eberhart type lime kilns.

The type of fuel used in kilns is one other important parameter that affects the lime quality. There is not much choice for both for producing high quality lime under economical conditions and satisfying the limit values for stack gas emissions. Various fuels are burned since B.C. 7000 and the fuels are used are liquid, solid and gas phases. Various coal types are used as kiln fuel in lime kilns that are established in various places of Anatolia since 1950s and due to price increases in petroleum and natural gas in 1983, 140 $/ton price for petroleum coke was not a reason for lime producers to stop using petroleum coke. While it is allowed to use this fuel, which has high calorific value and low ash ratio, in parallel flow Maerz type kilns after pulverizing which is very suitable for lime production is allowed for use in classical Eberhart type lime kilns only after considerable amount of changes are made on this type of kiln. It is clear that the petroleum coke, which is used in modernized Eberhart type kilns is loaded from top of the kilns without pulverizing together with the limestone so as to form a homogeneous thickness. Therefore, emission licenses are given after proving that the fuel remains for at least 0.3 s at 900 ºC and in this way carcinogenic PAHs have been annuled.

In addition to modifications made in the kilns, some modifications were also done on the stack systems. The most important modification is to pass the stack gases that are expected to form on top region of the kiln by soaking through heat-resistant region at 900 ºC that reaches up to calcination region. In this way, since carcinogenic PAHs that exist in the petroleum gas are annuled, the emission values are under the limit values. Due to treatment system that is mounted on the stack, both SO_2 and particulate matter emissions are seen to be reduced. Instantaneously high CO emissions within stack gas emissions result from inadequate amount of oxygen.

The petroleum coke was started to be used in Turkey and found widespread application areas after 1990. Traditional lime producers could not start research and development activities on the quality of lime they produce because for years they used domestic coal having calorific value of 4500-5000 kcal/kg, sulfur value of 4.0-4.5 % and ash value of 20-0 %. After the petroleum coke became available in the market, it was noticed to have calorific value of 7000-7500 kcal/kg, sulfur value of 3.5-4.0 % and ash value of 3-5 %, they reached a common opinion not to use any other type of coal. Due to high increase of the prices of petroleum coke and rapid increase in the use of domestic coal, the domestic use of petroleum coke was banned in 1996 by industry except large industrial facilities having fluidized bed kilns, gas treatment units and by cement and sugar factories. However, while retail the price of petroleum coke that could be imported by allotment in dimension of 0-20 mm was 40 $/ton in 1980s, its price now is 140 $/ton. Even the price of it so high, it is not expected from lime producers to give up using the petroleum coke.

What are the characteristics of good lime?

It does not matter which kiln is used for its production, the quality and place of use are important for the lime that will be offered to the market. Construction sector and iron-steel industry consume lime at different characteristics. Hydraulic lime production that is used for the restoration of archeological art structures with the addition of some additives to the kiln in the past 10 years became important in lime industry.

Quick lime samples that are produced with semi-automatic system in classical Eberhart type lime kilns in which some modifications are performed are picked up as soon as they come out of the kilns and brought to laboratory in plastic sample bags. Experiments are performed in Kelvin 1042 model Sorptometer apparatus using N_2 and He gases. The results obtained in these experiments are classified and the meanings of good lime, bad lime and average level lime are investigated.

Theoretically, in a normal calcination process, 44 % of $CaCO_3$ (100 %) must be discharged to atmosphere as CO_2 or CaO must be removed from system with a separate mechanism. No $CaCO_3$ is expected within the structure after calcination. But this expectation does not always become true in kiln conditions. Limestone $CaCO_3$ starts dissolving after 300 ºC and gets a porous structure by giving CO_2 within it to the medium and transformation is completed at 975 ºC. In practice, this does not happen all the time. There are various reasons for this. Non-homogeneous structure of limestone loaded to the kiln, non-effective calcination temperature at every point in the kilns, development of calcination process from the wall to the center and non-homogeneous particle dimension distribution of limestone prevent regular discharge of CO_2 from the mass. Although limestone charge to the modernized Eberhart kilns is provided in +40 mm and -80 mm dimensions with the help of a semi-automatic system, uniform kiln rock distribution can not be accomplished in practice. Therefore, while small particles complete calcination process when they reach 900 ºC and discharge CO_2 within them and take sponge-like structure, there might still be $CaCO_3$ within the core regions of the large particles. Since it is almost impossible to intervene with this situation under kiln conditions, it will be necessary to extend calcination time to allow complete calcination of large particles. In this case, CaO (quick lime) that completed the calcination process and that had sponge-like structure will remain under high temperature for a while and the opened pores will be closed back and it will be overcooked quick lime. The analysis performed showed that although loaded to the same kiln in the same party, quick lime at different characteristics was obtained due to non-homogeneous structure of limestone and non-uniform particle dimensions.

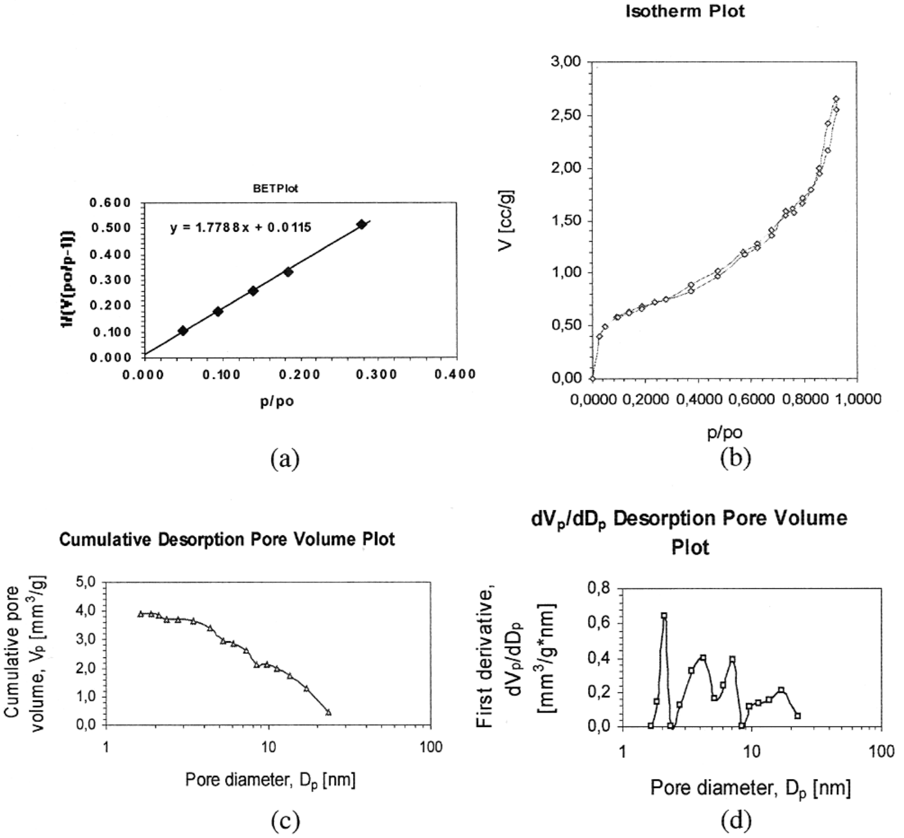
Full isotherm specific surface area measurements were performed on the samples that just came out of the kiln and that is classified physically as good lime, bad lime and average level lime based on the market conditions and the results are given in Table-10 in detail together with volume values that are absorbed at different pressures.

Based on these values, it was understood that the total porosity determined by the program of the apparatus is 4.09 mm^3/g. In addition, surface area, plot diagrams and size distribution of porosities obtained based on these data are given together in Fig. 5.

TABLE-10
POINT WISE ANALYSIS PERFORMED ON N1 QUICK LIME AND THAT ARE TAKEN AS BASIS FOR SPECIFIC SURFACE AREA MEASUREMENTS, POROSITY AND PLOT DIAGRAMS

Reactive pressure (p/po)	Volume adsorbed, V (cc/g)	Elapsed time (h:min)	Satur. Pressure, P_o (torr)
0.0000	0.000	–	–
0.0269	0.400	00:21	757.9
0.0484	0.484	00:32	757.8
0.0935	0.585	00:43	757.8
0.1393	0.635	00:56	757.7
0.1856	0.684	01:08	757.7
0.2797	0.752	01:19	757.3
0.3756	0.883	01:31	757.1
0.4739	1.022	01:42	756.7
0.5746	1.202	01:53	756.5
0.6258	1.273	02:04	756.3
0.6776	1.405	02:14	756.1
0.7301	1.550	02:25	755.8
0.7616	1.603	02:36	755.5
0.7942	1.710	02:46	755.4
0.8267	1.783	02:57	755.1
0.8593	1.942	03:07	755.1
0.8921	2.167	03:18	755.1
0.9249	2.543	03:29	755.0
0.9251	2.647	03:50	755.6
0.8923	2.423	04:13	755.8
08607	1.992	04:35	756.1
0.8283	1.790	04:58	756.2
0.7961	1.664	05:21	756.5
0.7636	1.576	05:45	756.7
0.7317	1.579	06:10	757.0
06794	1.353	06:36	757.2
0.6276	1.240	07:00	757.4
0.5762	1.169	07:25	757.5
0.4754	0.966	07:50	757.8
0.3768	0.830	08:16	758.0
0.2802	0748	08:45	758.1
0.2329	0.725	19:13	757.8
0.1859	0.658	19:41	757.6
0.1400	0.614	20:08	757.5
0.0940	0.580	20:37	757.5

Analysis log; Full isotherm (standard).



(a) (b)

(c) (d)

Fig. 5. Bet Plot diagram (a), Isotherm plot diagram (b), cumulative porosity plot diagram (c) and porosity size distribution (d) of the quick lime

When these diagrams are analyzed, it can be seen that the dimensions and distributions of the pores are quite homogeneous. The lime which is offered to the market as good lime and that has good characteristics in terms of its whiteness and porosity shall have plenty of pores in unit area, these pores shall be in close sizes to each other and active CaO per cent shall be above 90 %.

The same analysis was repeated for samples that are taken from the same kilns and that are considered to be bad lime on the market based on their appearance (NK1). In addition, when these samples are stifled in a glass container with water, it was seen that there are about 5 to 10 % substances that can not be dissolved in water. Total porosity was seen to be 2.57 mm^3/g for these samples and it was also seen that both the ratios of cumulative porosity volume to void dimensions and distribution of void size dimensions are more heterogeneous compared to good lime.

Conclusion

As a result, it can be concluded that both raw material quality and dimensions and calcination temperature and time is effective on lime quality. Total percentage of both surface area and porosity determined at the end of measurements in bad lime is determined to be either not opened at all or closed back although they were initially opened and therefore reduced relative to the good lime.

It was seen that by making some modifications in classical Eberhart type lime kilns, improvements can be accomplished in calcination conditions and similarly, some simple arrangements made in the stack system result in the drop of air polluting emission parameters to under limit values. The most important change made in the kilns is to increase the length of the kilns by 3.0-3.5 mm with cast armored, heat-resistant and recyclable ring system which extends from the top of the kilns down to the pit region and when carcinogenic PAHs emanating from petroleum coke pass through this region which is above 900 ºC, they are annulled. The elimination of problems for the petroleum coke that directly effects the lime quality and that has been an indispensable fuel for the past 15 years due to its high calorie and low ash content have created important advantages for lime producing industries which use classical Eberhart type lime kilns. In addition to above mentioned changes, upgrading loading and discharge operations to semi-automatic system, starting of weighing system and automation of parameter controls increased the production capacity by 20 %. Monitoring all these data from a control room and ability to preserve these data in computer environments are additional advantages.

The exhaust gas emissions discharged to atmosphere when the new system kilns operate in full capacity were measured before and after a gas treatment system is installed in the stack system and emission values of air pollutants were investigated comparatively with the limit values foreseen in the regulations. It was seen that particulate matter < SO_2 and NO_2 values were always under the limit values and CO values sometimes passes limit values but when the mass flow rates are taken as basis, it was seen that 50 kg/h limit values are always reduced. In addition, carcinogenic PAHs emanating from burning of petroleum coke as fuel must remain for at least 0.3 s above 900 ºC and it was proven with a scientific report prepared by TUBITAK (MAM) personnel based on measurement results that after the modifications performed, this condition is also satisfied. Under the light of this data, the partner company of this study, Nur Lime Company, is now in a position to obtain emission certificate for its 8 modified kilns from the Ministry of Environment and Forestry.

Chemical analysis were performed for pure limestone, dolomite type and clay-marl type limestone that are used as raw material for both kilns and in laboratory conditions and then lime was produced from them. Surface area and porosity measurements as well as active CaO determinations were done on quick lime and the relationship between calcination temperature and time is investigated in detail. Good lime and bad lime concepts were defined and by inspecting porosity ratios, porosity size distributions and their SEM images, the nature of calcination as temperature increases from 850 to 950 ºC depending on the level of pureness of limestone was analyzed. Based on this analysis, it was seen that pure limestone dissolves mostly up to 850 ºC and when temperature reaches to 900 ºC, dissolution reaches to maximum level and if the dissolved limestone stays longer under a temperature higher than this value, the opened pores are closed back. It was also seen that in dolomite type limestone, calcination starts at 650 ºC, depending on its MgO content and lasts up to 900 ºC. Since dolomitization within the raw material is diagenetic, it is seen that the pores that are opened in dolomitic sections are inclined to close back when temperature up to 900 ºC is necessary for the parts containing limestone to discharge their CO_2 completely. The situation is more complex in clay-marl type limestone that is included in a ratio of at most 5 % in kiln rocks and that can not be dissolved during operation and glass-like structures might form depending on the silica per cent. Therefore, it seems like it is very important to have a homogeneous kiln in order to be able to produce good lime.

Another important matter that was found out during this study is that active % CaO and surface area measurements and determination of porosity ratios must be performed on the lime as soon as it comes out of the kilns and the samples leaving the kilns must not be in contact with the atmospheric air. In humid place like Adana city, lime absorbs humidity in a short time and this result in porosity ratio defects.

It is important for the economy of the nation for the lime producers to modernize their classical Eberhart type lime kilns that have been used for lime production since 1950s and to continue their established powers for another 10-15 years. The assumption of some producers claiming that the lime of producers who use Eberhart type lime kilns, like Nur Lime Company, is not good do not reflect the truth since Eberhart type kilns are better than Maerz type kilns for obtaining more than 80 % CaO ratio (93 %) that is requested by especially iron-steel manufacturers. There is definitely a need for establishing good quality lime production facilities for producing lime that is needed for iron-steel industry which is founded or in the process of foundation in Payas-Iskenderun-Dortyol towns by Isdemir; Yazici, Ekinciler and Atakas groups. The need for lime will not end in this region where it is expected to be an iron gulf in the following 10 years. Therefore, it will be beneficial to modernized and develop classical Eberhart type lime kilns of the Anatolian lime producers.

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