

The Online Journal of Science and Technology

ISSN: 2146-7390

APRIL 2011 Volume 1 - Issue 2

Prof. Dr. Aytekin İşman Editor-in-Chief

Prof. Dr. Mustafa Şahin DÜNDAR Editor

Associate Prof. Dr. Galip AKAYDIN Associate Editor



Copyright © 2011 - THE ONLINE JOURNAL OF SCIENCE AND TECHNOLOGY

All rights reserved. No part of TOJSAT's articles may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Published in TURKEY

Contact Address: Prof. Dr. Aytekin İŞMAN TOJSAT, Editor in Chief Sakarya-Turkey

Message from the Editor-in-Chief

I am happy to inform you that the The Online Journal of Science and Technology (TOJSAT) has been published second issue in 2011. The first issue covered the selected papers from the conference which is entitled as International Science and Technology Conference. With the first issue online with selected papers from the conference, our journal opens an academic debate in contemporary education practices in respect to different fields.

In this respect, TOJSAT is interested in various researches in education in order to diffuse and share the knowledge with academic community.

The journal promotes knowledge sharing in the academic and professional agendas within multi-dimensional angles. Exploring professional issues through different research approaches allow researchers, practitioners and students to reconstruct knowledge from relevant theories and techniques. Therefore, I am pleased to publish second issue which different papers from various fields are shared with professionals.

And as you know TOJSAT will organize ISTEC 2011 (International Science and Technology Conference – 2011 <u>www.iste-c.net</u>) at Istanbul University between December, 7-9 2011. ISTEC series is an international educational activity for academicians and scientist. This conference is now a well known science and technology event. It promotes the development and dissemination of theoretical knowledge, conceptual research, and professional knowledge through conference activities. Its focus is to create and disseminate knowledge about science and technology.

We are pleased to announce that the presented papers at the International Science and Technology Conference 2011 will be reviewed for the January, 2012 and April, 2012 issues of TOJSAT.

Call for Papers

TOJSAT invites article contributions. Submitted articles should be about all aspects of science and technology. The articles should be original, unpublished, and not in consideration for publication elsewhere at the time of submission to TOJSAT.

April 01, 2011

Prof. Dr. Aytekin İŞMAN Editor-in-Chief of TOJSAT

Message from the Editor

OISAL

I am very glad to inform you that second issue of The Online Journal of Science and Technology (TOJSAT) has been published in 2011. The first issue of the journal covered the selected papers from the conference which is entitled as *International Science and Technology Conference*. With the first issue with selected papers from the conference, our journal opens an academic debate in scientific and technological practices in respect to different fields.

And as you know TOJSAT will organize ISTEC 2011 (International Science and Technology Conference - 2011) at Istanbul University between December, 7-9 2011. ISTEC conference series is an international science and technology activities for academicians, scientists, engineers, and educators. It promotes the development and dissemination of theoretical knowledge, conceptual research, and professional knowledge through conference activities.

I would thank all authors and associate editors on their great contributions to the second issue of TOJSAT.

April 01, 2011 Prof. Dr. M. Şahin DÜNDAR Editor, TOJSAT



Editor-in-Chief

Prof. Dr. Aytekin İŞMAN - Sakarya University, Turkey

Editor

Prof. Dr. Mustafa Şahin DÜNDAR - Sakarya University, Turkey

Associate Editor

Associate Prof. Dr. Galip AKAYDIN, Hacettepe University, Turkey

Editorial Board

Ahmet AKSOY, Erciyes University, Turkey Ahmet APAY, Sakarya University, Turkey Ahmet BİÇER, Gazi University, Turkey Ali DEMIRSOY, Hacettepe University, Turkey Ali Ekrem OZKUL, Anadolu University, Turkey Ali GUNYAKTI, Eastern Mediterranean University, TRNC Alparslan FIGLALI, Kocaeli University, Turkey Arif ALTUN, Hacettepe University, Turkey Aydın Ziya OZGUR, Anadolu University, Turkey Bekir SALIH, Hacettepe University, Turkey Belma ASLIM, Gazi University, Turkey Bilal GÜNEŞ, Gazi University, Turkey Bilal TOKLU, Gazi University, Turkey Cafer CELIK, Ataturk University, Turkey Ergun KASAP, Gazi University, Turkey Fatma ÜNAL, Gazi University, Turkey Gürer BUDAK, Gazi University, Turkey Harun TAŞKIN, Sakarya University, Turkey Hasan DEMIREL, Eastern Mediterranean University, TRNC Hikmet AYBAR, Eastern Mediterranean University, TRNC Hüseyin EKİZ, Sakarya University, Turkey Hüseyin Murat TÜTÜNCÜ, Sakarya University, Turkey Işık AYBAY, Eastern Mediterranean University, TRNC İbrahim OKUR, Sakarya University, Turkey İlvas ÖZTÜRK, Sakarva University, Turkey İsmail Hakkı CEDİMOĞLU, Sakarya University, Turkey Latif KURT, Ankara University, Turkey Levent AKSU, Gazi University, Turkey Mehmet Ali YALCIN, Sakarya University, Turkey Mehmet TURKER, Gazi University, Turkey Mehmet YILMAZ, Gazi University, Turkey Metin BAŞARIR, Sakarya University, Turkey Murat DIKER, Hacettepe University, Turkey Mustafa GAZI, Eastern Mediterranean University, TRNC

Mustafa GUL, Turkey M. Şahin DÜNDAR, Sakarya University, Turkey Nabi Bux JUMANI, Allama Iqbal Open University, Pakistan. Orhan ARSLAN, Gazi University, Turkey Orhan TORKUL, Sakarya University, Turkey Osman CEREZCI, Sakarya University, Turkey Rahmi KARAKUS, Sakarya University, Turkey Recai COŞKUN, Sakarya University, Turkey Recep ILERI, Sakarya University, Turkey Ridvan KARAPINAR, Yüzüncü Yıl University, Turkey Sevgi BAYARI, Hacettepe University, Turkey Süleyman ÖZÇELİK, Gazi University, Turkey Tuncay ÇAYKARA, Gazi University, Turkey Türkay DERELI, Gaziantep University, Turkey Ümit KOCABIÇAK, Sakarya University, Turkey Yusuf KALENDER, Gazi University, Turkey Vahdettin SEVINC, Sakarya University, Turkey Veli CELIK, Kırıkkale University, Turkey Zekai SEN, Istanbul Technical University, Turkey Abdülkadir MASKAN, Dicle University, Turkey Ahmet Zeki SAKA, Karadeneniz Technical University, Turkey Ali GUL, Gazi University, Turkey Atilla YILMAZ, Hacettepe University, Turkey Berrin ÖZÇELİK, Gazi University Can KURNAZ, Sakarya University, Turkey Eralp ALTUN, Ege University, Turkey Fatma AYAZ, Gazi University, Turkey Burhan TURKSEN, TOBB University of Economics and Technology, Turkey Galip AKAYDIN, Hacettepe University, Turkey Gilbert Mbotho MASITSA, University of The Free State - South Africa Gregory ALEXANDER, University of The Free State - South Africa Hasan Hüseyin ONDER, Gazi University, Turkey Hasan KIRMIZIBEKMEZ, Yeditepe University, Turkey Hüseyin YARATAN, Eastern Mediterranean University, TRNC Iman OSTA, Lebanese American Universiy, Lebanon Kenan OLGUN, Sakarya University, Turkey Mehmet CAGLAR, Eastern Mediterranean University, TRNC Muharrem TOSUN, Sakarya University, Turkey Murat TOSUN, Sakarya University, Turkey Mustafa DEMİR, Sakarya University, Turkey Mustafa GAZI, Near East University, TRNC Mustafa KALKAN, Dokuz Eylul Universiy, Turkey Nureddin KIRKAVAK, Eastern Mediterranean University, TRNC Oğuz SERİN, Cyprus International University, TRNC Selahattin GÖNEN, Dicle University, Turkey Senay CETINUS, Cumhuriyet University, Turkey

Sevgi AKAYDIN, Gazi University, Turkey Ali ÇORUH, Sakarya University, Turkey Antonis LIONARAKIS, Hellenic Open University, Greece Canan LACIN SIMSEK, Sakarya University, Turkey Cüneyt BİRKÖK, Sakarya University, Turkey Ercan MASAL, Sakarya University, Turkey Ergun YOLCU, Istanbul University, Turkey Elnaz ZAHED, University of Waterloo, UAE Fatime Balkan KIYICI, Sakarya University, Turkey Gülay BİRKÖK, Gebze Institute of Technology, Turkey Hasan OKUYUCU, Gazi University, Turkey Hayrettin EVİRGEN, Sakarya University, Turkey İsmail ÖNDER, Sakarya University, Turkey Melek MASAL, Sakarya University, Turkey Muhammed JAVED, Islamia University of Bahawalpur, Pakistan Mustafa YILMAZLAR, Sakarya University, Turkey Nilgun TOSUN, Trakya Üniversitesi, Turkey Nursen SUCSUZ, Trakya Üniversitesi, Turkey Phaik Kin, CHEAH Universiti Tunku Abdul Rahman, Malaysia Rıfat EFE, Dicle University, Turkey Senol BESOLUK, Sakarya University, Turkey Uner KAYABAS, Inonu University, Turkey Yusuf KARAKUŞ, Sakarya University, Turkey Yusuf ATALAY, Sakarya University, Turkey Yüksel GÜÇLÜ, Sakarya University, Turkey



Table of Contents

EFFECT OF MUNICIPAL HEATING SYSTEM COAL ASH ON THE INSULATION PROPERTIES OF LIGHT WEIGHT CONCRETE	1
Ali Yiğit, İsmail Demir, M .Serhat Başpınar	
A NUMERICAL INVESTIGATION OF MULTIPHASE FLOW AND OIL SPILL IN ISTANBUL STRAIT	8
Ali Doğrul, Yasemin Arıkan, Fahri Çelik	
CRITIQUES OF ADORNO AND HORKHEIMER ON MODERN SOCIETY: A PESSIMISTIC APPROACH	16
Burcu Yaman	
PRINCIPAL COMPONENT CHART FOR MULTIVARIATE STATISTICAL PROCESS CONTROL	22
Gafar Matanmi Oyeyemi	
STUDY OF SULFIDES MINERAL FLOTATION WITH XANTHATES: CONTROL PARAMETRES OF FLOTATION	32
Zohir Nedjar, Djamel Barkat, Mustapha Bouhenguel	

EFFECT OF MUNICIPAL HEATING SYSTEM COAL ASH ON THE INSULATION PROPERTIES OF LIGHT WEIGHT CONCRETE

Ali YİĞİT², İsmail DEMİR¹, M.Serhat BAŞPINAR¹

¹Afyon Kocatepe University, Technical Education Faculty, Ahmet Necdet Sezer Kampusü 1. Eğitim Binası -Gazlıgöl Yolu 03200-Afyonkarahisar-Turkey ²Hakkari University Vocational Training School, Hakkari-Turkey e-mail: idemir@aku.edu.tr

Abstract: Large quantities of coals have been used as fuel use for central heating system in Turkey. It has been causing a considerable waste that has been dumped into landfills. On the other hand enhanced construction activities, shortage of conventional building materials and abundantly available industrial wastes have promoted the development of new building materials. In this study, usage of coal ash as supplementary building material in light weight concrete was investigated. For this purpose, chemical analyses of the coal ash, perlite, and silica fume samples were determined. Lime was added to the coal ash as a binder. The binder (slaked lime) ratio was kept constant at 45% throughout this study. In order to get comparable results samples were prepared with five different compositions. Expanded perlite and silica fume added some mixtures.

After certain time of curing, physical and mechanical tests were conducted. It was concluded that, coal ash can be used economically for the production of lightweight building blocks (LWBB). Optimal strength-thermal conductivity combination was obtained by the usage of silica fume and expanded perlite together. Improved strength properties were obtained by using hydrothermal curing conditions and super plasticizer addition.

Keywords: Coal ash, silica fume, expanded perlite, lime, lightweight concrete blocks.

Introduction

Lightweight aggregates have higher water absorption rate and lower relative density according to normal aggregates. In addition to being light, it has good strength, fire resistance and heat insulation. Apart from the density of the aggregates, the density of the concrete also depends upon the grading of the aggregates, their moisture content, mix proportions, cement content, water-to-binder ratio, chemical and mineral admixtures, etc. Besides the material, it also depends upon the method of compaction, curing conditions, etc (Neville, 1987). The use of lightweight aggregate in concrete has many advantages, for examples; reduction of dead load, high thermal insulation, reduced the handling and transporting costs, improved the fire resistance etc.

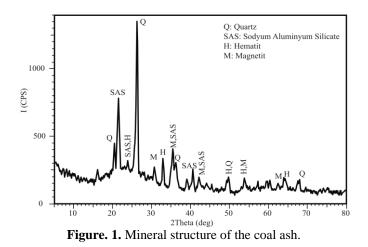
Lightweight concrete (LC) is generally used to reduce the dead weight of a structure as well as reduce the risk of earthquake damages. Earthquake forces that will influence the civil engineering structures and buildings are proportional to the mass of those structures and buildings. Thus, reducing the mass of the structure or building is of utmost importance to reduce their damage risk due to earthquake (Yaşar *et.al*, 2003). But perhaps the most significant potential advantage of the use of lightweight aggregates for concrete and building in general is the environmental value. When the raw materials needed for lightweight production are derived from industrial by products, the environment and economy of the producing locality and country are deemed to benefit. Housings are usually heated with central heating system in Turkey. Coal is used mostly as fuel. The resulting ash is usually collected in municipal solid waste depot. The aim of this study was to study the possibility of using coal ash as aggregate to manufacture cement free lightweight concrete block (LWCB) and determine the effects on the insulation properties.

Experimental

Municipal heating system coal ash was used in the study. Coal ash, expanded perlite and silica fume were taken from the solid waste storage in Afyonkarahisar city (Turkey), Etibank Perlite Enterprise in İzmir and Antalya Electro Metallurgy Enterprise in Turkey respectively. First furnace ash was milled in the porcelain ball mill. Furnace ash is appropriate to the C class according to ASTM C 618, since total oxide of $SiO_2+Al_2O_3+Fe_2O_3$ is 77.48% and CaO is less than 10% (Table 1). The mineral composition of the coal ash is mainly quartz, sodium aluminium silicate, hematite and magnetite (Figure 1). Commercial grade slaked lime was used as bonding material in the experiments. The chemical composition of the coal ash, expanded perlite and silica fume is given in Table 1. The particle size distribution of the fly ash, silica fume and expanded perlite was measured with Laser Size Distribution Analyzer-Master Sizer X1.2b (Figure 2).

Table 1. Chemical analyses of coal ash (CA), silica fume (SF) and expanded perlite (EP).

Oxides (%)	SiO ₂	Al_2O_3	Fe_2O_3	MgO	CaO	Na ₂ O	K_2O	TiO ₂	SO ₃	LOI	Total
Coal ash	51,90	18,18	7,40	1,75	1,17	0,72	1,32	0,4	2,35	9,55	94,74
Silica fume	87,66	0,42	0,64	3,77	0,89	0,29	0,31	0,01	-	3,70	97,68



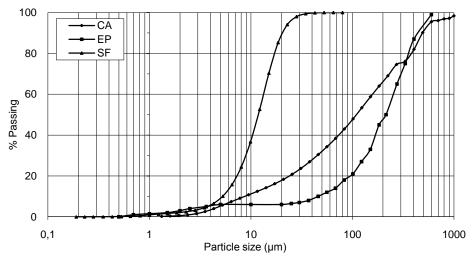


Figure. 2. The particle size distributions of coal ash (CA), silica fume (SF) and expanded perlite (EP).

Sample preparation and test methods

Five series samples were produced. The mix proportions of coal ash, silica fume, perlite and lime are given in Table 2. The mix proportions were prepared in condition of dry weights of the ingredients. The CaO/ SiO₂ ratio was adjusted on 1.6 to by weight all mixtures. Water was added to the mixture of dry materials and the water content was decided as defined below. The water to solid ratio was adjusted to obtain pastes of normal consistency. Then water/binder ratios were determined on test series for 75-80% by weight. Naphthalene sulphonate type superplasticizer was used of 0.7% of binder (lime) in the series, compatible with ASTM C 494.

		oportions c	i une sumpres	(
	А	В	С	D	E	
Coal ash	55	52.5	51.25	50	52.5	
Lime	45	45	45	45	45	
Silica fume	-	2.5	2.5	2.5	-	
Perlite	-	-	1.25	2.5	2.5	
W/B (%)	0.80	0.77	0.75	0.75	0.75	

Table 2. Mix proportions of the samples (in wt %).

Water was added to the mixture of dry materials. The water/binder ratio was adjusted to obtain pastes of normal consistency (TS EN 12350-2). Water/binder ratio was varied between 0.75% and 0.80% respectively. Slump was kept constant at 25 ± 5 mm. For each mixture, average 24 samples of 100x100x100 mm3 cubes were cast in to steel mould. The mixture was first mixed for 5 minute in a mixer and then placed in mould and it was properly compacted for 2 minute on a vibration table. After 24 hour, the specimens were taken out from the moulds and specimens were covered with moist bags for additional 48 hour. Afterward each group was divided into four parts. Steam curing treatment were applied the first part samples in a laboratory type autoclave for 6 hour. The autoclave has 20 liter volume and operated at 1.5 Bar pressure and at 120 oC temperature. Other series (2., 3. and 4.) specimens were cured for 7, 28 and 90 days respectively in a laboratory curing tank at 21 ± 2 oC , then removed and were put in an oven as far as constant weight obtained for tests. Physical and mechanical tests for each series were applied on at least 6

samples and the average value of the results was presented. Tests were performed for bulk density, apparent density, open porosity, and water absorption according to TS EN 992, TS EN 678 and TS 3624, respectively. Compressive strength test was applied in accordance with ASTM C 109 (TS EN 679). A quick thermal conductivity meter (Shotherm QTM-D2 Kyoto Electronics Manufacturing Co. Ltd., Japan) based on ASTM C 1113- 90 hot wire method was used to measure the thermal conductivity. For this purpose having dimensions of 100x50x17 mm samples were prepared. Measurement range of the test device is between 0.020 and 10 W/m.K. Measurements precision is $\pm 5\%$ of reading value each reference plate.

Results and Discussion

For the various mixes, the 28-day bulk density and the apparent density varied from 1.29 to 1.35 gr/cm³ and from 2.17 to 2.34 gr/cm³ respectively. Also, expanded perlite addition slightly lowered density of the samples. The density values are much lower than that of normal weight concrete (Table 3). Open porosity of the mixtures varied from approximately 38% and 44% while water absorption changed between 28% and 33%. For all series, addition of silica fume and expanded perlite increases the long term strength properties. It can be easily say that more reactive and finer additions caused an increase in the strength behaviour of the mixtures.

The property change of the series were compared the control series (A series). When the highly reactive silica fume was replaced instead of coal fly ash caused a decrease in the strength of the samples at B mixtures by autoclave curing (Table 3). However, silica fume replacement caused increase in the strength values at normal water curing condition. Highly pozzolanic silica fume addition may improves the expansive phase formation of Ettringite and causes a decrease in the strength at the early and fast hydration period during autoclaving condition. Strength loss due to the expansive Ettringite formation in the early hydration period was also explained by former researchers (Mulenga et al, 2003).

Replacing coal ash with only silica fume increased the bulk density, decreased the open porosity and led to increase in the thermal conductivity of the samples. This was mainly the fine particle size of the silica fume particle which filled the pores of the system. Increasing bulk density and formation of the crystalline Ettringite phase are the main possible reasons for the increase in the thermal conductivity. It has been reported that the crystalline structures show higher heat conduction than the amorphous structures.

	А	В	С	D	E
λ (W/mK)	0.55	0.52	0.56	0.58	0.57
Open porosity (%)	43.73	43.44	40.68	37.77	41.92
Bulk density (gr/cm ³)	1.31	1.32	1.31	1.35	1.29
Apparent density (gr/cm ³)	2.33	2.34	2.21	2.17	2.23
Water absorption (%)	33.39	32.83	30.53	27.96	32.45
NY 1 00001 / 3					

Table 3. Physical and mechanical properties of the test samples.

Normal concrete: 2300 kg/m³, λ :1.3 – 1.5 (W/mK)

6 Hour ac [*]	9.67	6.82	10.31	15.07	12.56
7 Day wc ^{**}	5.01	8.92	8.45	9.64	8.61
28 Day wc**	5.47	9.72	12.01	12.52	11.83
90 Day wc**	11.62	12.88	13.71	13.90	12.30

Table 4. Compressive Strength (MPa)

ac^{*}: Autoclaving curing, wc^{**}: Water curing

When comparing the 28 day water cured sample microstructures, it can said that A and D series sample's hydration microstructures were similar to each other (Figure 3). Replacing silica fume and expanded perlite together instead of fly ash decrease the open porosity and consequently increase the mechanical properties. From the microstructures, one can say that physical and mechanical property changes of the samples were independent from the hydration properties of the mixtures. Demirboğa et al (2001) and Karakoç (2004) reported that EPA (Expanded perlite aggregate) increased the compressive strength of light weight concrete.

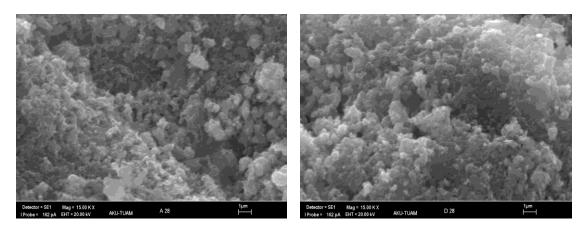


Figure 3. SEM microstructures of 28 day water cured A and D series samples.

Although the hydration properties of the different mixture pastes was same, there were regional structure differences between the series of samples (Figure 4). For example, in the control series (A series) unreacted large portlandite phases (plate like) were detected in the structure. It can be said that control series sample have lower pozzolanic reaction capacity than other series which contains silica fume and expanded perlite. Therefore free lime has not been consumed during pozzolanic reaction.

TOISAT

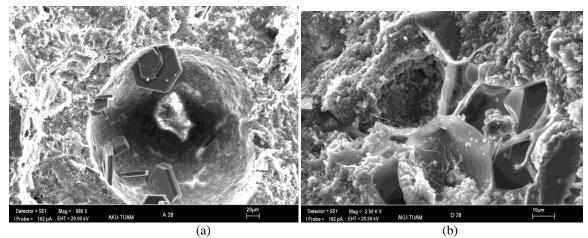


Figure 4. Regional structure variance of the samples (a: A sample series, b: D sample series).

Due to the closed pore structure of the expanded perlite (Figure 4.a), water absorption and open pores of the perlite containing samples were decreased. Greater decrease in the water absorption behaviour was observed when silica fume was added simultaneously (Table 3).

Conclusions

It was concluded from the study that; coal ash from municipal heating systems can be used to produce cement free light weight concrete blocks. Pozzolanic properties of the coal ash can be enhanced by the addition of other reactive additions such as silica fume. Addition of silica fume to coal ash + lime system improves the long term strength development of the system. In addition to the possible changes in the hydration properties of the mixtures by the additions, particle size differences between the coal ash and silica fume cause strength improvement. Finer silica fume particles filled the pores better and provides better compaction. Due to the pore structure of the expanded perlite, its addition did not influence the physical properties at a given addition rate. Expanded perlite addition by replacing coal ash was increased the strength properties.

References

ASTM C 109. Standard test method for compressive strength of hydraulic cement mortars. ASTM; 1993.

ASTM C 494. Standard specification for chemical admixtures for concrete. ASTM 1994.

ASTM C 618. Standard specification for coal fly ash and raw or calcined natural pozzolan for use a mineral admixture in

concrete. ASTM; 2003.

ASTM C 1113-90. Test method for thermal conductivity of refractories by hot wire (Platinum resistance thermometer technique).

Demirboga R, Orung I', Gul R. Effects of expanded perlite aggregate and mineral admixtures on the compressive strength of low-density concretes. Cement and Concrete Research 2001;31:1627–32.

Kayali O., Fly ash lightweight aggregates in high performance concrete, Construction and Building Materials 22 (2008) 2393–2399

Karakoc M.B. Effects of expanded perlite aggregate on physical and mechanics properties of high strength concrete. A Master's thesis, Department of Civil Engineering, Ataturk University, Erzurum, Turkey; 2004.



Neville AM, Brooks JJ. Concrete Technology. Longman Scientific and Technical; 1987. p. 188, 349.

Mulenga DM, Stark J, Nobst P. Thaumasite formation in concrete and mortars containing fly ash. Cement Concrete Compos 2003;25:907–12.

TS EN 678. Determination of the dry density of autoclaved aerated concrete, this standard specifies the procedure for the determination of dry density of autoclaved aerated concrete. Turkish Standards Institution (TSE); 1995.

TS EN 679. Determination of the compressive strength of autoclaved aerated concrete, This standard specifies the procedure for the determination of the compressive strength of autoclaved-aerated concrete, 1995.

TS EN 992. Determination of the dry density of lightweight aggregate concrete with open structure, this standard, specifies a method of determining the dry density of light weight aggregate concrete with open structure. Turkish Standards Institution (TSE) 1998.

TS 3624. Test method for determination the specific gravity the absorption water and the void ratio in hardened concrete, this standard specifies the test method for determination the specific gravity, the absorption water and void ratio in hardened concrete. Turkish Standards Institution (TSE); 1981.

TS EN 12350-2. Testing fresh concrete- Part 2: slump test, this standard specifies two procedures for sampling fresh concrete bycomposite sampling and by spot sampling. Turkish Standards Institution (TSE); 2002.

Yasar E, Atis CD, Kilic A, Gulsen H. Strength properties of lightweight concrete made with basaltic pumice and fly ash. Materials Letters 2003;57:2267–70

A NUMERICAL INVESTIGATION OF MULTIPHASE FLOW AND OIL SPILL IN ISTANBUL STRAIT

Ali Doğrul, Yasemin Arıkan, Fahri Çelik

Yildiz Technical University, Faculty of Naval Architecture and Maritime, Dept. of Naval Architecture and Marine Engineering 34349 Besiktas-Istanbul / TURKIYE e-mail: adogrul@yildiz.edu.tr

Abstract: Istanbul Strait is a globally important inland sea region connecting two continents. It is the most crowded and dangerous strait succeeding Strait of Malacca. Istanbul Strait's traffic density is 3 times of Suez Canal, 4 times of Panama Canal because of international sea traffic and this density is increasing every day, so it is becoming more dangerous. To decrease this danger, the flow in the strait must be investigated in a realistic way by using present opportunities.

In this study, a part of Istanbul Strait is modeled by a commercial CFD code and investigated numerically. The multiphase flow in the strait is analyzed and also oil spill is simulated for the same model. During the analyses, the currents in the strait and the sheer force caused by the wind are taken into account.

Keywords: Istanbul Strait, multiphase flow, oil spill, CFD.

Introduction

Istanbul Strait is 31 km long and approximately 50000 ships are passing through the strait every year. And average depth of the strait is 35, 8 meters. Winds coming from Black Sea and Mediterranean Sea are effective on the strait. The transition of the strait is difficult due to the waves and strong currents forced by these winds (Can, 1988).

The lack of vaporization in the Black Sea causes a level difference between the Black Sea and the Marmara Sea. This difference causes a pressure difference, so in Istanbul Strait, there is an up current from Black Sea to Marmara and there is a down current from Marmara to Black Sea. The reason of the down current is that the densities of the fluids are different (Baydar, 1994). The salinity of the up current is ‰ 18 and down current is ‰ 21.

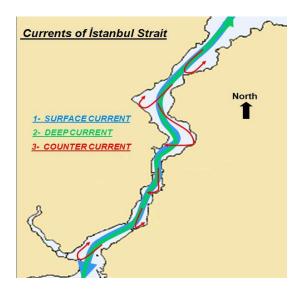


Figure 1. Currents in Istanbul Strait.



Figure 2. Salinity of Istanbul Strait.

The traffic in the strait is increasing so the amount of oil transportation is also increasing. In oil transportation Istanbul Strait is important because it is the only opening gate for the countries which have sea borders to Black Sea. For this reason the risk of pollution in Istanbul Strait is becoming more important. Oil is the most important

factor in sea pollution. Main reasons of sea pollution caused by oil are: tanker accidents, oil production in the sea, oil refineries, discharging of ballast water into the sea (Güven et al., 1998).

In fact, many accidents occurred in recent years in Istanbul Strait. And especially tanker accident had important effects on the strait.

	TOTAL	TOTAL	TRANSIT	TANF	KER	
MONTHS		GT		ТТА	LPG- LNG	ТСН
JANUARY	3949	36,435,114	2149	482	75	156
FEBRUARY	4029	36,594,659	2239	478	63	178
MARCH	4904	42,905,410	2636	582	75	190
APRIL	4890	43,233,610	2671	556	65	157
MAY	5014	44,366,542	2726	573	72	171
JUNE	4909	42,625,497	2761	576	59	187
JULY	5064	46,119,645	2975	588	66	186
AUGUST	4988	46,415,009	3140	549	55	164
SEPTEMBER	4570	43,710,510	2812	508	55	138
OCTOBER	4479	47,154,955	2798	575	61	140
NOVEMBER	3816	41,245,600	2367	518	62	157
DECEMBER	3784	42,829,063	2488	579	56	151
TOTAL	54396	513,635,614	31762	6564	764	1975

Table 1. Statistical data of ships passing Istanbul Strait (2009) (www.turkishpilots.org).

Table 2. Statistical data of ship accidents in Istanbul Strait, (Örs and Yılmaz, 2003).
--

YEARS	TOTAL	TANKER	CRASH	FIRE	LANDING	TOTAL
1996	49952	4248	2	0	5	7
1997	50942	4303	2	0	9	11
1998	49304	5142	3	0	8	11
1999	47906	4452	4	3	6	13
2000	48079	4937	5	0	4	9
2001	42637	5188	15	0	5	20
2009	54396	9303	39	11	27	77

Studies have been made for oil spill simulation around the world for years. Some researchers use their own CFD codes and methods instead of commercial ones. Reed et al. (1999) has given brief information about many models used in studies between 1990 - 1999. One of them is the dispersion model based on the experimental work of Delvigne and Sweeney which has now become a standard. This method estimates the entrained oil mass per unit area as well as unit time, and is used by plentiful researchers.

Nakata et al. (1997) presented the equations for a two-layer, two dimensional system for a Nakhodka tanker oil spill by using the model developed by Yapa et al. (1994). Sugioka et al. (1999) investigated the tanker accident "Diamond Grace" with "Lagrangian discrete panel" method. Skognes and Johansen (2004) simulated oil spill given from a point with the help of StatMap model which is including wing data of the region. Elliott and Jones (2000) simulated the oil spill in Liverpool Bay with "particle tracking" model in three dimensions. Hansen and Ditlevsen (2003) solved oil spill problem occurred after tanker accidents with the program GRACAT (Grounding and Collision Analysis Toolbox). The GRACAT program is an integrated software package developed at the Technical University of Denmark from 1998 to 2001. Wang et al. (2005) used particle method for two dimensional oil spill problem. Sebastiao and Soares (2007) tried to calculate the instabilities in oil spill prediction.

There are also some studies for oil spill simulation in Istanbul Strait. Örs and Yılmaz (2003) developed a numerical model for oil spill problem in the strait. This model solves shallow water equations in accordance with finite element method. Can (2007) also simulated oil spill for the strait and determined critical regions. Ertürk and Yonsel (2002) analyzed oil spill problem with Dirichlet boundary conditions by using ADAM model. Beji et al. (2008) investigated the two phase flow in Istanbul Strait numerically. The two phase flow was examined by Can (1988). An oil spill with multiphase flow and exhaust simulation are made by Dogrul (2010).

In literature, generally simulations are made in two-dimensional. Present study differs from previous studies by analyzing a local part of Istanbul Strait (Rumeli Kavağı – Beykoz) for oil spill with two-phase flow in 3-dimendional. Firstly the multiphase flow is analyzed and the interaction between the currents is observed. After that an oil spill is simulated with multiphase flow in the strait. In these analyses, wind effects and currents on the sea surface are taken into account.

Mathematical Model

3-D working domain (Fig .3b) was meshed by GAMBIT, the preprocessor of FLUENT. This domain represents a local part of the strait, Rumeli Kavağı - Beykoz, as seen in Fig. 4. Mostly dangerous part of the strait is around Rumeli Kavağı - Beykoz region.

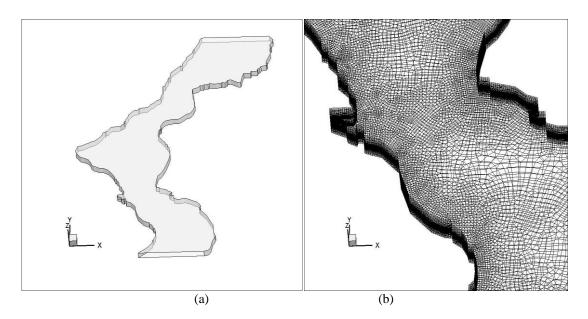


Figure 3. 3-D geometry (a), mesh structure applied to the model (b).

Copyright © 2011 - www.tojsat.net

As can be seen from Fig. 3, unstructured mesh elements have been generated for the simulations. Because of multiphase flow in the strait, a fine mesh structure is used near the plane between two phases. Mesh element number is about 1.3 million.

Both sides of the strait are specified as wall type and bottom surface of the whole domain is considered as wall, too. Uniform velocity, turbulent kinetic energy (k) and turbulent dissipation rate (ϵ) are given at the inlet surfaces, while pressure outlet is specified at the outlet surfaces. The solver considered here uses finite volume method as discretization scheme. The flow is unsteady, incompressible, and three-dimensional. With the help of unsteady simulations, interaction between two phases is observed and later oil spill is simulated.

For the mathematical model the time-averaged, three-dimensional, unsteady-state mean flow equations of continuity and momentum can be written in Cartesian tensor notation as;

$$\frac{\partial \rho}{\partial t} + div \left(\rho. \vec{V} \right) = 0 \tag{1}$$

$$\rho \frac{DU_i}{Dt} = -\delta_{ij} \frac{\partial P}{\partial x_j} + \mu \frac{\partial^2 U_i}{\partial x_j^2} \tag{2}$$

As turbulence closure, standard k- ε (SKE) turbulence model with standard wall-function is used. The SKE turbulence model is one of several two-equation models that have developed over the years. It is probably the most widely and thoroughly tested of them all. As it is well known that SKE is a semi-empirical model based on model transport equations for the turbulence kinetic energy, k (Eq.3) and its dissipation, ε , (Eq. 4)

$$\frac{\partial\rho k}{\partial t} + \frac{\partial(\rho u_i k)}{\partial x_i} = \frac{\partial}{\partial x_i} \left[\left(\mu + \frac{\mu_t}{\Pr_k} \right) \frac{\partial k}{\partial x_i} \right] + \mu_T G - \rho \varepsilon + S_{k,p}$$
(3)
$$\frac{\partial\rho \varepsilon}{\partial t} + \frac{\partial(\rho u_i \varepsilon)}{\partial x_i} = \frac{\partial}{\partial x_i} \left[\left(\mu + \frac{\mu_T}{\Pr_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_i} \right] + \frac{\varepsilon}{k} \left(C_1 \mu_T G - C_2 \rho \varepsilon \right) + S_{\varepsilon,p}$$
(4)

where C1 and C2 are additional dimensionless model constants; Prk and Pre are the turbulent Prandtl numbers for kinetic energy and dissipation, respectively; Sk,p and Se,p are source terms for the kinetic energy and turbulent dissipation; and the turbulent production rate (G) is defined in Eq. 5:

$$G = \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \frac{\partial u_i}{\partial x_j} - \frac{1}{\rho^2} \frac{\partial \rho}{\partial x_j} \frac{\partial \rho}{\partial x_J} - \frac{2}{3} \left(\frac{\rho k}{\mu_T} + \frac{\partial u_i}{\partial x_J}\right) \frac{\partial u_J}{\partial x_j}$$
(5)

In FLUENT 6.2, the governing equations are discretized using a first-order upwind interpolation scheme, and the discretized equations are solved using PISO algorithm. As the multiphase model, "mixture" is chosen. Typical relaxation factors used here is 0.3, 0.7, 0.8, 0.8 and 0.2 for pressure, momentum, turbulence kinetic energy, turbulence dissipation rate and volume fraction. The related equations are solved for flow, turbulence and volume fraction. The

solution is seen converged when the continuity residual is lower than 10-7 and residuals of other variables are lower than 10-6.

As the boundary conditions; mostly same conditions are applied to both models; multiphase model and oil spill model. Boundary conditions are given in Table 3 and 4.

) ent	Black Sea inlet	Velocity Inlet
Up current	Marmara inlet	Pressure Outlet
vn ent	Black Sea inlet	Pressure Outlet
Down current	Marmara inlet	Velocity Inlet
	Side walls	No Slip Wall
	Bottom	No Slip Wall
	Surface	Slip Wall

Table 3. Boundary conditions applied to multiphase model.

Table 4. Boundary conditions applied to oil spill model.

ıt	Black Sea inlet	Velocity Inlet
Up current	Black Sea mier	versenty milet
l Cul	Marmara inlet	Pressure Outlet
<i>м</i> п ent	Black Sea inlet	Pressure Outlet
Down current	Marmara inlet	Velocity Inlet
	Side walls	No Slip Wall
	Bottom	No Slip Wall
	Surface	Slip Wall
	Oil inlet	Velocity Inlet

In all analyses, lower level depth and upper level depth is considered as 20 and 30 meters respectively. Up current velocity is 0.3 m/s and down current velocity is 1.3 m/s. Density of the up current is 1018 kg/m3 while down current density is 1021 kg/m3 as shown in Figure 2. For all simulations, the wind is considered as coming from north and its velocity is accepted as 1 m/s. So the surface shear force caused by the wind is calculated as 0.0006925 Pa (Eq. 6) and applied to the sea surface.

$$\tau_{w} = 1.25 c_{d} W^{2}$$
 (6)

The density of the oil used in the analysis is 960 kg/m3. It is considered that totally 50000 m3 oil is spilled to the sea during the analysis. Oil inlet velocity is 0.01 m/s. So the oil is spilled for 1600 seconds, then the dispersion of the oil is observed for some time.





Figure 4. Investigated part of the strait.

Results

As mentioned above, the main goal of this study is to simulate multiphase flow and oil spill in Istanbul Strait. To achieve this goal series of computational analyses are performed on a personal computer of four dual-cores of 2.8 GHz with 6 GB RAM. After reaching the convergence criteria some results are obtained in following figures.

Figure 5 and 6 show counter currents as mentioned above.

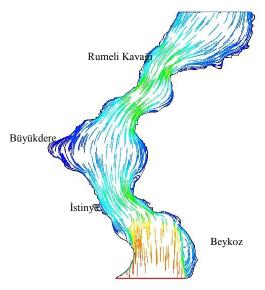


Figure 5. Counter currents on the surface.

OISAI

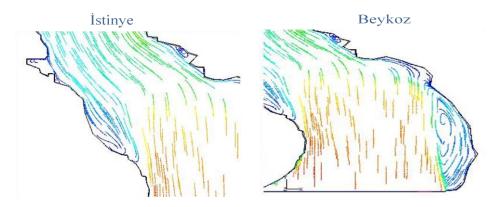


Figure 6. Counter currents in İstinye and Beykoz.

Volume fraction of oil on the surface is investigated in oil spill simulation and all analyses are made with transient calculation to obtain the behavior of spilled oil. The counter currents are seen in Figure 5 and 6.

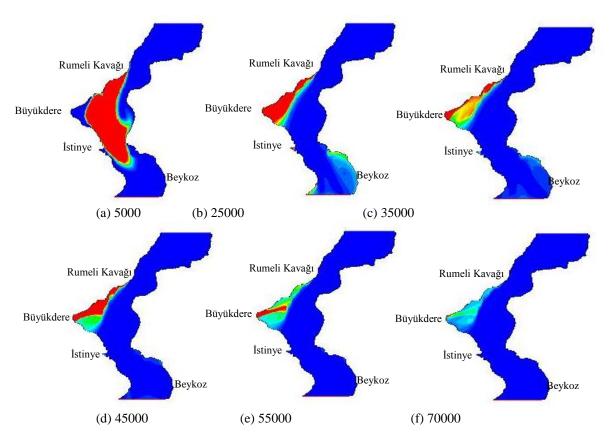


Figure 7. Behavior of spilled oil at time steps 5000, 25000, 35000, 45000, 55000, 70000 s.

In Figure 7, the results of simulation are given. In this simulation, which oil started to spill from Rumeli Kavağı, it is seen that at about 5000 s the oil started to collect in Büyükdere area. And between 5000 and 25000 s, the spilled oil flowed to the south direction due to the wind and currents.

But even in 70000 s some oil still collected in Büyükdere area. The simulation showed that in case of an accident in Rumeli Kavağı, the oil is collected in Büyükdere area.

The present study can be considered as an initial study for the preparation of the contingency plan of Istanbul Strait. similar oil spill simulations can be carried out for different areas of the strait to guess the risks in Istanbul Strait in case of sea pollution due to accident scenarios.

Conclusion

Istanbul Strait is important in oil transportation and the safety of the strait is also important. In this study, an important area of the strait is investigated for an oil spill in case on a tanker accident with two-phase flow in 3-dimensional. Unlike the previous studies, the domain is simulated in 3-dimensional and all the currents in the strait are taken into account. Also wind effects are simulated in the analyses.

According to the results, a tanker accident in Rumeli Kavağı area can be dangerous for the strait and city of Istanbul. So by using these simulations, an emergency plan should be made for the safety of Istanbul.

References

Baydar, M., (1994), *Climate Conditions of Istanbul Strait and Near Regions*, MSc Thesis, Istanbul University, Institute of Marine Science and Management, Istanbul, 91.

Örs, H. and Yılmaz, S. L., (2003), Oil Transport in the Turkish Straits System: A Simulation of Contamination in the Istanbul Strait, Energy Sources, 25 (11): 1043-1052.

Can, S., (1988), *Investigation of Two Phase Flow in Istanbul Strait*, BSc Thesis, Istanbul Technical University, Department of Naval Architecture, Istanbul.

Dogrul, A., (2010), *Numerical Investigation of Shipborne Pollution in Istanbul Strait*, MSc Thesis, Yıldız Technical University, Institute of Science, Istanbul.

Güven, K. C., Unlu, S., Okus, E. et al. (1998), The Oil and Anionic Surfactant Pollutions in Seawater of *Turkish Straits in 1995-1997*, The Proceedings of the First Int. Sym. on Fisheries and Ecology, 1: 403-409, Trabzon.

http://www.turkishpilots.org

Fluent Inc. Gambit 2.2 User's Guide, Fluent Inc., 2005

Fluent Inc. Fluent 6.2 User's Guide, Fluent Inc., 2005

Reed, M., Johansen, O. et al. (1999), *Oil Spill Modeling Towards The Close of The 20th Century: Overview of The State of The Art*, Spill Science & Technology Bulletin 5 (1), 3-16.

Delvigne, G.A.L. and Sweeney, C.E., (1998), *Natural Dispersion of Oil*, Oil and Chemical Pollution 4, 281-310.

Nakata, N., Sugioka, S. and Hosaka, T., (1997), *Hindcast of A Japan Sea Oil Spill*, Spill Science & Technology Bulletin 4 (4), 219-229.

Yapa, P.D., Shen, H.T. and Angammana, K., (1994), *Modeling Oil Spill In A River System*, Journal of Marine Systems 7, 453-471.

CRITIQUES OF ADORNO AND HORKHEIMER ON MODERN SOCIETY: A PESSIMISTIC APPROACH

Burcu Yaman

İzmir Ekonomi University, Sakarya Cad. No:156 35330 Balçova-İzmir/Turkey burcu.yaman@ieu.edu.tr

Abstract: Critical Theory that has been developed by Frankfurt School is one of the most important schools of thought that criticizes modern society with a Marxist manner but at the same time they differentiate themselves from classical Marxist approach in some aspects. In this paper, the critiques of Max Horkheimer and Theodor Adorno towards modern society will be covered with the light of their article of Culture Industry; Enlightenment as a Mass Deception. The discussion will mainly cover the bringing of modernity including Enlightenment era with its rational, instrumentalist and positivist manner and also culture industry which is one of the most criticized aspect of capitalist order by them. Their critiques of culture industry will be analyzed in more details and it will help us to see how Critical Theory has a more pessimistic approach than classical Marxism in terms of understanding and evaluating modern world that is surrounded by a manipulated culture industry.

Keywords: Enlightenment, Modernity, Culture Industry

Introduction

The modernity or modern society that cannot be separated from reason, science, technology, progress and positivism has been considered by some philosophers as the emancipation of humankind especially with arise of "Enlightenment" that is thought as the end of irrational but the beginning of liberated man. However, the modernity and the enlightenment with their enormous consequences have not been celebrated by all of the thinkers that they have been the centre of accusations for the problematic aspects of society and the system. Critical Theory developed by Frankfurt school, is one of the important school of thought that criticize the modern society with a Marxist manner but at the same time they differentiate themselves from Marxist approach in some aspects. In this paper, the critiques of Max Horkheimer and Theodor Adorno towards modern society and enlightenment will be covered with the light of their books of Dialectic of Enlightenment. During this discussion, how they are differentiating from Marx and how they have a pessimistic tendency about the social transformation will also took place as an important issue.

To start with brief information about the formation of Frankfurt school seems to be better in order to understand historical background of the ideas of Adorno and Horkheimer taking place especially in Dialectic of Enlightenment. David Held also emphasize that "In order to grasp the axes around which critical theory developed it is essential to understand the turbulent events which were at the roots of its founders' historical and political experience."(1980:16). Frankfurt Institute for Social Research that was founded in 1923 in Germany is the actual school associated with Frankfurt school. In the first sense, the Institute is known as an interdisciplinary Marxist school of social theory, however the Institute appears with the claim that traditional Marxism isn't able to explain the capitalism of twentieth century and also they are highly critical about the Soviet socialism. From this point, the school develops a theory named as critical theory that differentiates them from traditional and scientific theories. In 1930, Max Horkheimer becomes the director of Institute but in these years fascism in Germany also gets more powerful that in 1933 Hitler achieves to come to power. The rise of fascism in Germany and Soviet socialism make the social theorists of Frankfurt school to see that traditional Marxism failed in the prediction of any revolution in a capitalist society, instead they experience how the workers suppressed and how there is a great popular support for fascism and also how Soviet socialism is turning into a totalitarianism with violence. As a result of this fascist pressure in Germany, they have to move the Institute to USA until the reestablishment of it in Frankfurt in 1953.

Critiques of Modern Society

As it is stated before, the critique of modern society and enlightenment is one of the central points of critical theory that most of the social theories from this school of thought have written on this from different aspects and approaches. As it is expected, Adorno and Horkheimer, coming from critical theory approach, tries to create a portrait of modern society from a radical perspective. Their critiques of modern society starts with a traditional Marxist approach by engaging with capitalism and its exploitation but also their critique has some other dimensions. The Enlightenment and its bringing of reason and rationality or positivism put into the center of critiques. Also, they go further of Marxism and focus on not only capitalism but cultural structure of modern society is examined deeply to see how the domination is consolidated over society. In the following part of the paper, Adorno and Horkheimer's portrait of modern society will be tried to drawn by examining their critiques of the capitalism, culture industry and Enlightenment. By examining each of the concepts, we will try to see how they rationalize their claims , but most important thing is we will try to answer the question of whether there is a possibility of emancipation from the capitation and domination of these systems by seeing how they differ from Marx in that sense.

In the critiques of Adorno and Horkheimer on modern society and modernity, it is better to start with the concept of Enlightenment that they mostly associate with modern system. In this sense, it can be easily said that Dialectic of Enlightenment, written by Adorno and Horkheimer, is one of the most important texts to understand their view of Enlightenment and modern society. The book, as a text of critical theory, briefly tries to demonstrate that how the modern society with its capitalist system and Enlightenment itself created domination over individuals although it promised the freedom. According to them, the enlightenment that they define as "Enlightenment, understood in the widest sense as the advance of thought, has always aimed at liberating human beings from fear and installing them as masters." (2002: 1) started with the promises that the reason and new way of positivist approach help people to release from their slavery by using their reason; however Enlightenment could not achieve this because besides to its promises what Enlightenment brought created another myth that is domination over individuals by exposing instrumental system. In the Dialectic of Enlightenment, Adorno and Horkheimer tries to shows how Enlightenment is actually a myth for domination in different sections such as; "Myth is already enlightenment, and enlightenment reverts to mythology" (2002: xviii) and in another place as "Enlightenment's program was disenchantment of the world. It wanted to dispel myths to overthrow fantasy with knowledge."(2002: 1). As these statements shows that they were suspicious about what Enlightenment brought and gifted to modern society.

Firstly, it is better to mention about the positivism that is promoted by the Enlightenment era and anti-positivist approach of critical theory. Positivism that is based on epistemological view highly depends on the objectivity and the facts derived from natural sciences. In positivist approach, the subjectivity is denied as not being a fact and social facts are ignored. In that point the positivism is started to be criticized especially by Weber and then Frankfurt School theorists. Firstly, by Frankfurt school and Horkheimer, positivism is seen as a kind of reduction because everything is tried to be explained by natural sciences. Another point of critique is that positivism admits the knowledge that is easily visible in objective world as fact, and those that can be generalized, so this approach can not explain social relations and facts. Second critique is about the suppression that is created by positivism, because critical theory claims that positivism prevents any challenging action with because of its conservative manner about the knowledge and facts. Since positivism only depends on facts, it only reproduces the status quo without giving any room for challenge and reflection toward society. In the book of Raymond Geuss, he states about it as: "Positivism is no particular obstacle to the development of natural science, but is a serious threat to the main vehicles of human emancipation, critical theories. One basic goal of the Frankfurt School is the criticism of positivism and the rehabilitation of 'reflection' as a category of valid knowledge." (1981:2).

Another point that Adorno and Horkheimer criticize is 'instrumental reason' that gets more powerful with increasing rationalization process in modern societies. In instrumental reason and rationalization process, people starts to make decision based on more rational choices that they only consider the efficiency and make always calculations about what a decision or action will bring to them. This leads to ignorance of morality of means to reach the end. As Weber, critical theorists see this as a product of modern societies, because the instrumental reason serves for capitalism, modern science and modern state. In capitalism for example, it is important to give rational decision and it is legitimized to use every means for the interest or the end that is aimed. In the discussion of culture industry of Adorno and Horkheimer that will take place in the following part of the paper, instrumental reason is a critical aspect of system. According to them, the rationality and instrumentality of modern societies have also conquered the culture, because the value of a cultural product depends on whether it has any purpose or it is a mean of something else. In the Dialectic of Enlightenment, this is mentioned as "Everything is perceived only from the point of the view that it can serve as something else, however vaguely that other thing might be envisaged." (2002: 128). Moreover, in terms of science and technology, the instrumental reason is a key because these concepts are based on this instrumentality and claims that manipulation and control of nature is essential and rational. The instrumentalization of nature is also criticized for being an idea of Enlightenment as Rolf Wiggershaus states "They (Frankfurt School) wanted to blame the disaster on Enlightenment, but again and again blamed it on a form of enlightenment qualified as bourgeois, as domination over nature and so on..." (1995: 333). However, in that point we see that critical theorists claim that this instrumental reason now also starts to control and manipulate human nature, because it becomes a part of social life. In that point, we see that theorists refers to the Weber's iron cage concept that means rationality creates a system similar to iron cage and people can not emancipate from this cage because it is attached to their lives and dominated all of the society. David Held mentions about this subject as follows:

They shared Weber's view as to the probability of the continuing expansion of rationalization and bureaucratization. They also shared his pessimism as to the dangers and risks involved which Weber called the 'iron cage' of a highly bureaucratized division of labor. The extension of formal means-end rationality to 'the conduct of life' becomes a concern as a form of domination: means becoming end, social rules becoming reified objectifications commanding directions. (1980:66).

The concept of 'culture industry' developed by Adorno and Horkheimer and explained in detail in their book of Dialectic of Enlightenment, is crucial and significant concept for understanding the critiques of them toward modern society and capital system. Culture industry term is used by them for the new form of cultural artifacts in capitalist world. This term is chosen intently instead of mass culture in that way in order to emphasize how the culture becomes a commodity in modern world. Their critique of mass culture is interpreted as "For the first time, popular culture was attacked from a radical rather than a conservative direction" by Martin Jay (1996:217). The technological developments and capitalist system created such a system and monopoly that dominated the culture and individuals. In Dialectic of Enlightenment, Adorno and Horkheimer tell "No mention is made of the fact that the basis on which technology acquires

power over society is the power of those whose economic position in society is strongest. A technological rationality is the rationality of domination" (2002: 95)

The first characteristic of culture industry is its mass production style. In that style, all of the cultural products are produced in masses like a commodity by losing all of its value. In this system, all cultural artifacts faces with the fact of being all same like a principle and as it is stated in as "Culture today is infecting everything with sameness.... Each branch of culture is unanimous within itself and all are unanimous together." (2002:94). In this system, standardization and massification becomes the key points that all of the products lack of any imagination of audiences and ends of all products are easily predictable since they serve for and reproduce the status quo. The culture only produce and reproduce the world we everyday perceive and it duplicates the outside world. People who consume the products of culture industry can not distinguish them from reality because they are trained to identify them with reality without questioning. (2002:100). All of the products of culture industry are also structured and produced for easy consumption, by this way they penetrate in all phases of life without making itself so much disturbing and noticeable. This characteristic of culture industry creates inertia in society according to Adorno and Horkheimer because people get used to consume everything easily so they lose their potentiality to question and broader perception of world. The amusement of culture makes all people sleep in their routines of lives, they are only prepared to the other day that they will serve for capitalist world. This situation leads to a great conformism in society also and it is a significant critique of Adorno and Horkheimer about the modern society. As it is stated before, system demands the obedience and conformism of society. However, it does not do this apparently that it says you can think and behave different than system, but when it happens, it pushes them out of the society and labeled as 'other'. Anyone who does not conform is condemned to an economic impotence which is prolonged in the intellectual powerlessness of the eccentric loner." (Adorno, Horkheimer, 2002: 106). This hidden suppression coming from the requirement of conformism also aims to abolition of individuality and any form of objection and resistance. In this modern capitalist system, culture industry takes the power of individual and presents a new pseudo-individuality to deceive them. The individuality and self also becomes a monopoly product of culture that all uniqueness of the individual is lost. However, the most important aspect of this situation is that not the attempt of culture industry to abolish individuality but also acceptance of society. It is the fact that the most critical and crucial part of the culture industry for Adorno and Horkheimer is the attitude of society and individual towards the domination and enslavement of culture industry. People do not resist but instead they conform because they like the easiness and comfortableness of the culture industry. Adorno and Horkheimer criticize it by stating that "They insist unwaveringly on the ideology by which they are enslaved. The pernicious love of the common people for the harm done to them outstrips even the cunning of the authorities." (2002: 106). The reason of lack of resistance is showed as the capitalist system surrounding the society because they can not go out of the system, and the worst thing they even do not want to go out of it as Adorno and Horkheimer said "Capitalist production hems them in so tightly, in body and soul, that they unresistingly succumb to whatever is proffered to them." (2002: 106). They also become a part of the system and strongly attached to it. This system is so well organized for deception that it does not remain any room for the emancipation and people resign and dedicate themselves to the continuity of the system. It is told in the book as "...but the necessity, inherent in the system, of never releasing its grip on the consumer, of not for a moment allowing him or her to suspect that resistance is possible." (2002: 113).

Although Adorno and Horkheimer are coming from Marxist approach, they did not remain in the same place and a transition from Marx in some extent occurred in their Critical Theory. In general, they follow the Marxist view for explaining the system by emphasizing on capitalist system, its exploitation and class struggles, but their political and historical experiences show that in practice especially Marxism failed to response to the modern society. David Held explains this transition as "Following Marx, they were preoccupied, especially in their early work with the forces which moved society towards rational institutions- institutions which would ensure true, free and just life. But they were aware of the many obstacles to radical change and sought to analyze and expose these." (1980: 15) They were thus concerned both with interpretation and transformation The first point that they contradict with Marx is his conception of history and idea of progress. When we look at the Marx's conception of history, we see that he believes there is progress in history. He claims briefly and basically that history has stages in itself and in these stages the classes derived from mode of production conflicts with each other and this struggle leads to the revolution and to the transformation of a new stage. This materialistic conception of history is however not shared by Adorno and Horkheimer as other Frankfurt school theorists. They think that this understanding of history does not work because there is no such a progress coming from the struggle. Martin Jay indicates the views of Frankfurt school on that "The hope for a radical transformation of conditions, indeed, any confidence in the possibility of historical progress at all, seemed to be without substance." (1996: 228). The denial of the progress by Adorno and Horkheimer differentiate them from Marx in another subject; that is the hope for revolution. Since there is progress in history and the stages are transformed by the revolutions for Marx, this means that Marx claims the current capitalist system will be replaced with socialism and at the end communism. In this sense, Marx believes that it will be achieved with the revolutionary potentiality of working class, especially in developed capitalist societies. However, Adorno and Horkheimer does not agree with this, because they think there is no more revolutionary potentiality of working class in this modern system of capitalist societies. The reason why they do not approve Marx is their experiences in their times. In these years, Adorno and Horkheimer witnesses that there is no tendency of revolution in working class, instead there is a great support for fascism especially in Germany. The working class loss its potential for revolution in Western capitalist societies with the suppression and domination of capitalist system, and even they starts to conform status quo." (Martin Jay, 1996: 228) The prediction of Marx about the place of revolution appears to be incorrect because the only revolution takes place in Russian Empire that is not a developed capitalist Western state. This revolution is seen as the actualization of Marxist theory by many, but Frankfurt school also criticizes it by seeing as a kind of totalitarian and authoritarianism that is similar to instrumentality of positivism. This positivist tendency of Soviet socialism is seen as legitimization of violence and a new form of oppression. However, besides to all of these differences, the most important difference is the pessimistic tendency of Adorno and Horkheimer according to Marx.

Conclusion

Until to this point, we see the critiques of Adorno and Horkheimer on the modern society by referring the Enlightenment, capitalist system and its culture industry and also their reinterpretation of Marx in some subjects. All of the critiques and claims showed that they believes we are all dominated and captivated by this iron system of modern society supported by capitalism and Enlightenment ideas. Now, it is time to answer to the question of whether it is possible for Adorno and Horkheimer to be emancipated from this domination by a social transformation. Although it is not easy to give an absolutely true answer, we can derive from their works that they are so pessimistic about such emancipation. They believe that there is highly no way for resistance and transformation. Here it can be better to rationalize their pessimism by rewording some discussions above. Firstly, the instrumental reason that is the product of Enlightenment is getting more powerful in the modern societies that it creates as Weber suppose a iron cage, and Adorno and Horkheimer believes that it is not possible to overcome this rationalization because it is in the all part of our lives and it is highly supported by capitalist system. Secondly, the culture industry of capitalist system increases their pessimism, because they observe that the culture industry not only deceives people but also dominates them by preventing any resistance. In culture industry, they see the system is perfectly organized for the enslavement of individual and suppression of society, but as stated before, the worst thing is the fact that people conform to that system because of inertia and love to not to resist this easy consumable culture. Also their criticism of traditional Marxism is another crucial point in their pessimism. As it is told before, they do not believe any progress in the history and possibility of revolution as Marx claims, since they see how the working class loses its potential to revolve and failure of Soviet socialism in the practice of Marxism. As Martin Jay indicates "A growing satisfaction with Marxism, even in its Hegelianized form, led him as it had Horkheimer and Adorno to examine the psychological obstacles in the path of meaningful social change. Whereas in their cases it strengthened a deepening pessimism and helped foster a retreat from political activism, in his, it led to a reaffirmation of the utopian dimension of his radicalism." (1996: 107). In short, the pessimism of Adorno and Horkheimer caused by the reasons mentioned above does not include so much real possibility for emancipation and any social transformation.

References

Adorno, T. W. with Max Horkheimer. (2002). *Dialectic of Enlightenment*. Stanford: Stanford University Press,

Geuss, Raymond (1981). The idea of a critical theory: Habermas and the Frankfurt school. Cambridge University Press.

Held, David (1980). Introduction to critical theory: Horkheimer to Habermas. University of California Press.

Jay, Martin (1996). The Dialectical Imagination: A History of the Frankfurt School and the Institute for Social Research. University of California Press.

Wiggershaus, Rolf. (1995). The Frankfurt School: Its History, Theories and Political Significance. Cambridge, MA: MIT Press

PRINCIPAL COMPONENT CHART FOR MULTIVARIATE STATISTICAL PROCESS CONTROL

Gafar Matanmi OYEYEMI Department of Statistics, University of Ilorin, Ilorin, Nigeria email: gmoyeyemi@gmail.com

Abstract: Multivariate statistical process control technique (Hotelling T^2 chart) was used to monitor four correlated quality characteristics (active detergent, moisture content, bulk density and ph level) of detergent produced by a company which indicated out-of-control signal. Principal Component Chart is used as a follow-up to out-of-control signal of the Multivariate Control Chart, to identify the quality characteristic(s) that contributed to the signal. The component scores obtained from the principal component analysis of the four quality characteristics measured were used to identify the quality characteristic(s) that contributed to the out-of-control signaled by the Hotelling T^2 chart. The chart of the first component which accounted for 96.7% of the total variability and has moisture content highly loaded in it is out-of-control, which implied that moisture content of the detergent produced by the company is out-of-control.

Keywords: principal components, out-of-control, quality characteristics, control limits, eigen-values

Introduction

Statistical process control is based on a number of basic principles which apply to all processes, including batch and continuous processes of the type commonly found in the manufacture of bulk chemicals, pharmaceutical products, specialist chemicals, processed foods and metals. The principles apply also to all processes in service and public sectors and commercial activities, including forecasting, claim processing and many financial transactions. One of these principles is that within any process variability is inevitable (Chanda, 2001).

Generally there are two groups of statistical process control (SPC), i.e. univariate statistical process control (USPC) and multivariate statistical process control (MSPC), which are used for different scenarios. The process of monitoring and control primarily apply to the systems or processes from the univariate perspective, which has only one process output variable or quality characteristic measured and tested. If a process is to meet or exceed customer expectations, generally it should be produced by a process that is stable or repeatable. More precisely, the process must be capable of operating with little variability around the target or nominal dimensions of the producer's quality characteristics.

Typically process monitoring applies to systems or processes in which only one variable is measured and tested. There are many processes in which the simultaneous monitoring or control of two or more quality characteristics is necessary. Process monitoring problems in which several variables are of interest are called Multivariate Statistical Process Control (MSPC). One of the disadvantages of a univariate monitoring scheme is that for a single process, many variables may be monitored and even controlled. MSPC methods overcome this disadvantage by monitoring several variables simultaneously. Using multivariate statistical process control methods, engineers and manufacturers who monitor complex processes may monitor the stability of their process.

The first original study in multivariate quality control was introduced by Hotelling (1947). Three of the most popular multivariate control statistics are Hotelling T^2 , Multivariate Exponentially-Weighted Moving Average (MEWMA) and the Multivariate Cumulative Sum (MCUSUM). The multivariate charts mentioned above take the correlations among the variables into account in monitoring the mean vector or variance-covariance matrix (Runger and



Montgomery, 1997). Multivariate charts are less popular than univariate charts because of the following reasons;

- The difficulty involved in their computation.

- Unlike univariate case, the scale of the values displayed on the multivariate chart is not related to the scales of any of the monitored variables.

- Once an out-of-control signal is given by the multivariate chart, it may be difficult to identify which of the variables caused the out-of-control signal. More complicated operations are required to determine the cause of the signals.

Multivariate control charts, such as Hotelling's- T^2 Control chart, Multivariate Exponential Weighted Moving Average (MEWMA) chart, Multivariate Cumulative Sum (MCuSum) chart, are used for monitoring several quality characteristics measured simultaneously on a product or process. Multivariate charts are also useful for monitoring quality profiles as discussed by Woodall et al. (2004). The objective of multivariate control charts is in two phases;

To identify shifts in the mean vector that might distort the estimation of the in-control mean vector and variance covariance matrix, and

- To identify and eliminate multivariate outliers. (Williams et al. 2006)

Alt (1995) defined two phases in constructing multivariate control charts, with Phase I divided into two Stages. In the retrospective Stage 1 of Phase I, historical data (observations) are studied for determining whether the process was in control and to estimate the in-control parameters of the process. The Hotelling's- T^2 Control chart is utilized in this stage (Alt and Smith, 1998, Tracy et al. 1992, and Wieda, 1994). In phase II, control charts are used with future observations for detecting possible departures from the process parameters estimated in Phase I. In Phase II, one uses charts for detecting any departure from the parameter estimates, which are considered in the in-control process parameters (Vargas, 2003).

An important aspect of the Hotelling's-T² Control chart is how to determine the sample variance-covariance matrix used in the calculation of the chart statistics (UCL and LCL). When rational subgroups are taken, the implication is that the appearance of a special cause of variation within a subgroup is unlikely, so that all observations within a subgroup share a common distribution. Thus, the regular sample variance-covariance matrix is useful and taking the average over all the subgroups is the common procedure, unless there are special causes that alter the variance-covariance matrix. If subgroups are taken and the population parameters are known then the Hotelling's T² statistic, T_i^2 , is $\chi^2_{\alpha,p}$ distributed, where p is the number of variables and α is the probability of false alarm. In the event that the population parameters are unknown (that is, the mean vector and the Variance-covariance matrices are unknown), the estimates are obtained from the sample and the Hotelling's T² statistic, T_i^2 , has an F or Beta distribution (Kolarik, 1999).

Construction of Hotelling's T² Control Chart

A set of n sub-samples of m observations collected are used in computing the control limits of the Hotelling's T² Control chart. For the observation x_{ij} , i = 1, 2, 3, , , m and j = 1, 2, 3, , , n, the Hotelling's T² statistic is obtained as follows; If the true parameters of a probability distribution are known, the χ^2 distribution is appropriate. Suppose that $x_1, x_2, x_3, , x_p$, are the variables from a normal distribution process and $\mu_1, \mu_2, \mu_3, , , \mu_p$ are the population means of the variables. $\bar{x}_1, \bar{x}_2, \bar{x}_3, , \bar{x}_p$ are the sample means, under assumption of knowing the variance-covariance matrix Σ , where

The statistic $T^2 = n(\bar{x} - \mu)' \Sigma^{-1}(\bar{x} - \mu)$ follows a chi-square (χ_p^2) with p degrees of freedom. Monitoring and detecting the out-of-control points depends on constructing correct control limits. The upper control limit (UCL) for the chart is given;

$$UCL = \chi^2_{\alpha,p}$$

When the true population values are not known, the statistics are computed using the estimates of the population parameters. The variance-covariance matrix Σ is estimated by the simple average of the m samples variance-covariance matrices;

The upper control limit (UCL) of the Hotelling T^2 chart is given by;

 $UCL = \frac{(m-1)^2}{m} B_{\left(\alpha, \frac{p}{2}, \frac{m-p-1}{2}\right)}, \text{ where } \alpha \text{ is the probability of false alarm for each}$

point plotted on the control chart, and $B_{\left(\alpha,\frac{p}{2},\frac{m-p-1}{2}\right)}$ is the (1- α) percentile of the beta distribution

with parameters u_1 and u_2 (Tracy et al. 1992, Wierda, 1994). The Hotelling T or F-distribution table may be use to obtain the Upper Control Limit (UCL). The Lower Control Limit (LCL) is always set to zero. The values of T_i^2 are plotted on the Hotelling T² chart, and if one of or more of the m points are out-of-control, special causes of variation are sought.

Although the knowledge of the statistical distribution of the control chart statistic is needed to calculate the upper and the lower control limits of the chart and estimate the control chart performance which are unknown in most cases. If the exact distribution is unknown or intractable, most especially when there are no subgroups, the upper control limit, UCL can be calculated from either an approximate distribution or from a Monte Carlo simulation (Williams et al. 2006). Although the T^2 chart is the most popular, easiest to use and interpret method for handling multivariate process data, and is beginning to be widely accepted by quality engineers and operators, it is not a panacea. First, unlike the univariate case, the scale of the values displayed on the chart is not related to the scales of any of the monitored variables. Secondly, when the T^2 statistic exceeds the upper control limit (UCL), the user does not know which particular variable(s) caused the out-of-control signal.

With respect to scaling, we strongly advise to run individual univariate charts in tandem with the multivariate chart. This will also help in honing in on the culprit(s) that might have caused the signal. However, individual univariate charts cannot explain situations that are a result of some problems in the covariance or correlation between the variables. This is why a dispersion chart must also be used.

Another way to analyze the data is to use *principal components*. For each multivariate measurement (or observation), the principal components are linear combinations of the standardized p variables (to standardize subtract their respective targets and divide by their standard deviations). The principal components have two important advantages:

The new variables are uncorrelated (or almost)

Very often, a few (sometimes 1 or 2) principal components may capture most of the variability in the data so that we do not have to use all of the p principal components for control.

Unfortunately, there is one big disadvantage: The identity of the original variables is lost! However, in some cases the specific linear combinations corresponding to the principal components with the largest <u>eigenvalues</u> may yield meaningful measurement units. What is being used in control charts are the principal factors. A principal factor is the principal component divided by the square root of its eigenvalue.

Principal Component Chart

One of the problems of multivariate control chart (Hotelling T^2 chart) is the problem of identifying the variable(s) that cause out-of-control signal in the chart. Because of its complexity in nature it is difficult to identify the variable(s) caused out-of-control signal, except constructing univariate control chart for each of the variables which posses another problem in the sense that the studied quality characteristics are believed to be highly correlated. Principal components can be used to investigate which of the p variables in the multivariate control chart are responsible for out-of-control signal. The most common practice is to use the first k most significant components, if Hotelling T^2 control chart gave an out-of-control signal, for further investigation.

The basic idea is that the first k principal components can be physically interpreted, and named. Consequently, if the Hotelling T^2 chart gives an out-of-control signal and, for instance, the second principal component chart also gives an out-of-control signal, then from the interpretation of this component, a direction to the variables which are suspect to be out-of-control can be deduced (Jackson, 1991). The discovery of the assignable cause of the problem, with this method, demands a further knowledge of the process itself, from the practitioner. The basic problem is that the principal components do not always have a physical interpretation.

The principal components are those uncorrelated linear combinations Y_1, Y_2, \ldots, Y_p , whose variances are as large as possible. Suppose the original dataset X is a p dimensional normal vector with mean and variance-covariance matrix given by μ and Σ respectively. The density of X is constant on the μ centered ellipsoids

$$(x-\mu)^{1}\Sigma^{-1}(x-\mu)=c^{2}$$

Which have axes $\pm c \sqrt{\lambda_i e_i}$, i = 1, 2, ..., p, where the pair (λ_i , e_i) are the eigenvalueeigenvector pairs of Σ . The c statistic is well-known in the literature as the Hotelling T² statistic. According to Johnson & Wichern (2002)

$$c^{2} = x^{1} \Sigma^{-1} x = \frac{1}{\lambda_{1}} (e_{1}^{1} x)^{2} + \frac{1}{\lambda_{2}} (e_{2}^{1} x)^{2} + -, -, - + \frac{1}{\lambda_{p}} (e_{p}^{1} x)^{2}$$

Where $e_1^1 x, e_2^2 x, -, -, -, e_p^1 x$ are the principal components of X. Setting $y_1 = e_1^1 x, y_2 = e_2^1 x, -, -, -, y_p = e_p^1 x$, we have

$$c^{2} = \frac{1}{\lambda_{1}} (y_{1})^{2} + \frac{1}{\lambda_{2}} (y_{2})^{2} + -, -, - + \frac{1}{\lambda_{p}} (y_{p})^{2}$$

In this way, the Hotelling T^2 statistic can be expressed as a function of the X values or as a function of the Y values (The components). Recommendations for selecting an appropriate number of principal component variables for multivariate statistical process control are typically the same as those proposed for traditional Principal Component Analysis in which the objective is to summarize a complex dataset. Following some guidelines suggested by Runger & Alt (1996):

Choose k such that
$$\sum_{i=1}^{k} \lambda_i \ge 0.9 \sum_{i=1}^{p} \lambda_i$$

Increment k such that
$$\lambda_i \ge \lambda_m$$
, where $\lambda_m = \frac{\sum_{j=1}^p \lambda_j}{p}$ and $i = 1, 2, -, -, k$

- Plot λ_i against i and select k at the "knee" in the curve.

Although these are useful guidelines in general, process control has a different objective than a summary of variation in a random sample of in-control data. Because the goal of statistical process control is to detect assignable cause in a stream of data collected over time, an approach to principal component analysis is to investigate the performance of a control chart as a function of k. Assuming we want 99.7% confidence interval, the Upper Control Limit (UCL), Center Line (CL) and the Lower Control Limit (LCL) are given in equation (1).

$$UCL = +3\sqrt{\lambda_{K}}$$

$$CL = 0$$

$$LCL = -3\sqrt{\lambda_{K}}$$
(1)

Multivariate Control Chart

The used is a secondary data and it consisted thirty-five single samples of detergent produced by a detergent company were randomly taken at regular interval. Four quality characteristics of the detergent were measure and they are x_1 (active detergent), or x_2 (moisture content) or x_3 (bulk density) or x_4 (ph level). Since single sample was taken at a time, that is, the sub-sample size n = 1; m=35. Hotelling T² control chart for individual observation is used to monitor the four quality characteristics of detergent produced by the company. The Mahalanobis distances are obtained using equation (2), the distances are then plotted to obtain the control chart for the detergent produced.

$$d_{1,i}^{2} = \left(x_{1i} - \bar{x}_{1}\right)^{1} S_{1}^{-1} \left(x_{1i} - \bar{x}_{1}\right) \quad i = 1, 2, 3, , , 48 \qquad ------(2)$$

The summary statistics are given as follows;

OISAT

$$\bar{x} = \begin{bmatrix} 23.3377\\ 3.4197\\ 309.4537\\ 10.4520 \end{bmatrix} \qquad S = \begin{bmatrix} 1.3021 & -0.1217 & 1.5289 & -0.0222\\ -0.1217 & 0.1066 & -1.5065 & -0.0418\\ 1.5289 & -1.5065 & 147.4957 & 0.0783\\ -0.0222 & -0.0418 & 0.0783 & 0.0865 \end{bmatrix}$$
$$R = \begin{bmatrix} 1.0000 & -0.1217^* & 0.1103^* & -0.0663\\ 1.0000 & -0.3798^{**} & -0.4349^{**}\\ 1.0000 & 0.0219\\ 1.0000 \end{bmatrix}$$

* Significant at 0.1 ** significant at 0.05

The correlation matrix shows that there exists inter-correlation among the four quality characteristics hence the reason for using multivariate control chart. The data as well as the mahalanobis distances are shown in appendix I. The Upper Control Limit (UCL) for the chart is given as follows;

$$UCL = \frac{(m-1)^2}{m} B_{\left(\alpha, \frac{p}{2}, \frac{m-p-1}{2}\right)} = 8.7181;$$
 where m = 35 and p = 4.

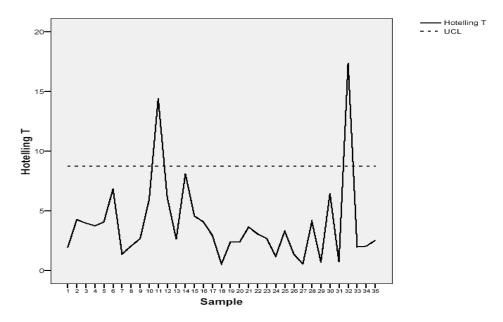


Figure 1. Hotelling T^2 chart for detergent produced by the company

Principal Component Charts

According to the multivariate control chart (Hotelling T^2 chart), the process producing the detergent was found to be out-of-control at 0.05 level of significance as shown in figure 1. One of the drawbacks of multivariate control charts is the identification of variable(s) that contributed to the out-of-control signal. From the chart, it is not possible to categorically say that either x_1 (active detergent), or x_2 (moisture content) or x_3 (bulk density) or x_4 (ph level) or any combinations of the four quality characteristics contributed to the out-of-control signal.

To identify which of the quality characteristics responsible for the out-of-control situation in the Hotelling T^2 chart, principal component analysis was use to obtain new components (PC1, PC2, PC3 and PC4) for the dataset (equation 3). These four components, PC1, PC2, PC3 and PC4 are linear combinations of the original variables (quality characteristics) and they are uncorrelated with one another. The component scores were then obtained from the linear combinations (components).

 $PC1 = a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + a_{14}x_4$ $PC2 = a_{21}x_1 + a_{22}x_2 + a_{23}x_3 + a_{24}x_4$ $PC3 = a_{31}x_1 + a_{32}x_2 + a_{33}x_3 + a_{34}x_4$ $PC4 = a_{41}x_1 + a_{42}x_2 + a_{43}x_3 + a_{44}x_4$

The component scores are treated as expected observations for each of the datasets, which are used to obtain a control chart. The quality characteristics will have different weight (eigen-vector) in each of the four components and if such component is out-of-control when plotted, then the variable that has highest weight will be concluded to have contributed to the out-of-control signal experienced in the Hotelling T^2 chart. The control limits of the principal component charts are given in equation (1), where λ_k is the eigenvalue of each of the components.

The Component Charts

Because of the different units in measuring the four quality characteristics, the characteristics were standardized by making use of their correlation matrix. The eigen-values and components matrix of the principal components analysis for the four quality characteristics given below;

It can be seen that while the second quality characteristic, x_2 (moisture content), is highly loaded in the first component (PC1), it is x_4 (ph level) for the second component (PC2), it is third quality characteristic, x_3 (bulk density) in the third component (PC3) and x_1 (active detergent) in the fourth component (PC4). Since the first component (PC1) accounted for about 96.7% total variability, it is therefore sufficient to make use of it in principal component chart. The component scores are obtained using the component matrix and the 99.7% control confidence limits (control limits) are obtained as follows;

$$UCL = +3\sqrt{3.8695} = 3.8939$$

 $CL = 0$
 $LCL = -3\sqrt{3.8695} = -3.8939$

The principal component chart is shown in figure 2

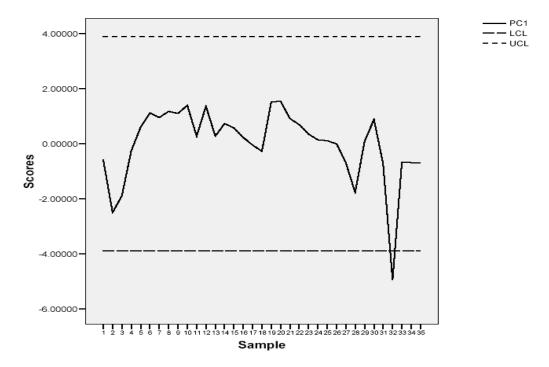


Figure 2. Principal component chart for the first component (PC1)

Discussion and Conclusion

The correlation analysis shows that there exist inter-correlation among the four quality characteristics monitored, hence the need for multivariate statistical process control technique. Hotelling T² control chart signaled an out-of-control for the product (detergent) based on the four quality characteristics by having samples 11 and 32 above the upper control limit. The principal component chart for the first component (PC1) also signaled an out-of-control with sample 32 falling below the lower control limit. The only characteristic that is highly loaded though negatively in the first component is x_2 (moisture content) can therefore be concluded that contributed to the out-of-control signal by the multivariate control chart.

The use of principal component chart has assisted in identifying variable(s) that contributed to the out-of-control signal given by the Hotelling T^2 chart. An individual Shewart control chart for each of the four quality characteristics would have been needed to monitore the four quality characteristics. And since the four quality characteristics are significantly related, the individual Shewart control chart will definitely not give convincing results. It is shown in this work that when a multivariate control chart signals an out-of-control, principal component chart



can be used to identify which of the monitored quality characteristic(s) contribute to the out-ofcontrol signal.

References

Alt, F. B. (1995). Multivariate Quality Control in Encyclopedia of Statistical Sciences 6 New York, John Wiley & Sons.

Alt, F. B. & Smith, N. D. (1998). Multivariate Process Control. Handbook of Statistics, P. R. Krishnaiah and C. R. Rao (eds). North-Holland Elsevier Science Publishers B. V., 7, 333-351

Chanda, M. J. (2001). Statistical Quality Control. CRC Press, LLC, 2000 N.W. Corporate Blvd., Boca Raton, Florida 33431

Hotelling, H. (1947). Multivariate Quality Control. Techniques of Statistical Analysis. McGraw-Hill

Jackson, J. E. (1991). A User Guide to Principal Components. John Wiley & Sons, N.Y.

Johnson, R. A. & Wichern, D. W. (2002). Applied Multivariate Statistical Analysis. Prentice Hall.

Kolarik, W. J. (1999). Creating Quality: Process Design for Results. McGraw-Hill International Edition. Singapore, McGraw-Hill Book Company.

Runger, G. C. & Alt, F. B. (1996): Choosing principal components for multivariate statistical process control. Communications in Statistics: Theory and Methods, 25, 909-922.

Runger, G.C. & Montgomery, D.C. (1997) Multivariate and univariate process control: geometry and shift directions. Quality and Reliability Engineering International, 13, 153-158.

Tracy, N. D., Young, J. C. & Mason, R. L. (1992). Multivariate Control Charts for Individual Observations. Journal of Quality Technology, 24, 88-95.

Vargas, J. A. (2003). Robust Estimation in Multivariate Control Charts for Individual Observations. Journal of Quality Technology, 35(4), 367-376

Wieda, S. J. (1994). Multivariate Statistical Process Control- Recent Results and Directions for Future Research, Statistica Neerlandica, 48, 147-168.

Williams, J. D., Woodall, W. H., Birch, J. B. & Sullivan, J. E. (2006). Distribution of Hotelling's T² Statistic Based on the Successive Differences Estimator. Journal of Quality Technology, 38(3), 217-229.

Woodall, W. H., Spitzner, D. J., Montgomery, D. C. & Gupta, S. (2004). Using Control Charts to Monitor Process and Product Quality Profiles. Journal of Quality Technology, 36, 309-320

Appendix

x						
sa	mple	detergent	moisture	density	ph level	distance
	1	22.23	3.65	315.45	10.47	1.9110911
	2	22.27	3.90	295.05	10.03	4.2494428
	3	22.34	3.67	289.64	10.24	3.9452862
	4	21.49	3.53	314.67	10.70	3.7194520
	5	22.26	3.43	325.58	10.70	4.0488209
	6	23.23	3.46	334.35	10.66	6.8160043
	7	23.58	3.22	322.86	10.41	1.3518301
	8	23.44	3.12	324.20	10.41	2.0275244
	9	23.35	3.24	329.04	10.43	2.6469698
	10	23.73	3.01	330.92	10.16	5.9341587
	11	25.81	3.75	300.94	10.80	14.4046455
	12	25.27	3.28	305.63	10.86	6.1193951
	13	22.53	3.20	300.87	10.72	2.6055144
	14	22.05	3.23	300.15	11.21	8.0851934
	15	22.34	3.16	299.69	10.94	4.5429742
	16	22.12	3.32	301.42	10.94	4.0531837
	17	22.70	3.23	296.70	10.61	2.9029115
	18	23.65	3.48	302.00	10.47	0.5197853
	19	23.16	2.97	318.79	10.63	2.3841190
	20	23.31	2.96	319.00	10.60	2.3574296
	21	25.41	3.22	305.60	10.43	3.6242317
	22	25.21	3.35	306.80	10.48	3.0371474
	23	24.69	3.24	303.08	10.29	2.6625240
	24	23.99	3.29	303.97	10.35	1.1557459
	25	23.61	3.16	301.34	10.29	3.2802867
	26	23.57	3.28	301.16	10.40	1.3501598
	27	23.38	3.57	306.78	10.25	0.5282338
	28	24.06	3.92	297.73	10.10	4.0879491
	29	24.01	3.49	308.99	10.47	0.6733271
	30	23.81	3.47	336.54	10.32	6.4455951
	31	22.59	3.57	309.78	10.32	0.6917973
	32	20.44	4.71	291.88	10.01	17.3669976
	33	23.51	3.54	312.13	10.05	1.9585475
	34	23.67	3.50	307.60	10.06	2.0075102
	35	24.01	3.57	310.55	10.01	2.5042148
	00	21.01	0.01	010.00	10.01	2.00 121 10



STUDY OF SULFIDES MINERAL FLOTATION WITH XANTHATES: CONTROL PARAMETRES OF FLOTATION

Zohir Nedjar¹, Djamel Barkat¹, Mustapha Bouhenguel² ¹Mouhamed Khider University, Biskra, Algeria ²Laboratories of Applied Chemistry and Technology of Materials «LACTM», Larbi Ben M'Hidi Oum El Bouaghi University, Algeria e-mail: zohirnedjar@gmail.com

Abstract: The flotation of sulphide minerals and their modulation has been a subject of investigation for many years. The influence of pH, D_p , D_b and xanthate concentration on the sulfide minerals floatability of is well known and it is usually used as one of the flotation control parameters.

In this study, we propose to make a theoretical and experimental study concerning the use of xanthate in the sulfides flotation processes (PbS-ZnS-FeS₂). Sphalerite (D_p = 0,4443mm, D_b =0,1530mm) floted in pH range from 7-10.5 but galena (D_p = 0,3705mm, D_b =0.2000 mm) floted better only from pH 8 to 9.5.

Keywords: Flotation, Sulphide Minerals, Xanthate, Pulp

Introduction

Flotation is a process of separation the mineral species which makes profitable the differences in their surfaces hydrophobia. The fundamental separation mechanism depends on the adsorption of an aqueous solution having properties on surfactant.

Flotation uses properties of minerals surface in order to return some of them selectively either hydrophobic subjects or absorbent. The ore, crushed is put in the form of pulp (mixture of particles and water) and contact with bubbles of air in agitated tanks known as: flotation cells. [1-2]

A large variety of chemical reagents is used, mainly to modify surface qualities of the particles. A significant amount of water is also necessary; the concentrated ore pulp is thickened, dried and sent in the metallurgical circuit of transformation (metal case of ore).

The interaction enters the metal sulphurized with xanthate is done by:

Chemical adsorption for the xanthic ion X⁻

 $X^- \rightarrow X_{ads} + \acute{e}$

Xanthate reaction with sulphurized metal (MS) to produce metal xanthate (MX_n)

$$MS + nX^{-} \rightarrow MX_{n} + S^{0} + n\acute{e}$$

$$MS + nX^{-} + 4H_{2}O \rightarrow MX_{n} + SO_{4}^{2-} + 8H^{+} + (6+n)\acute{e}$$

Xanthate oxidation to the dixantogene (X_2) on mineral surface

$$2X^- \rightarrow X_2 + 2\acute{e}$$



We choice the diagrams of flotation of oxidized and mixed ores lead-zinc depend on the report/ratio and the character of the ores lead-zinc and the existence of iron sulfide.

The ultimate goal of the regulation is not only to stabilize a process but also to optimize it and to increase economic efficiency by it. We could reach a regulation of an elevated level in the case of some concentrators, but success is still limited, because optimization can be realized only in factories that circuits reached a real balance [3-4].

Equilibrium equation particle -air bubble under the flotation conditions:

The analysis of the forces acting during the fixing of the particle on the air bubble shows that the particles density is considerably different (water - particles).

In flotation foams about it the acting forces are:

- The flotation.force.
- The centrifugal force.

$$F_f = P_m \cdot \gamma_{\lg} \cdot \sin\theta \tag{1}$$

$$F_c = \rho_s \cdot V_m \cdot \gamma_c \tag{2}$$

*P*_m : absorptivity Perimeter (cm);

 γ_{lg} : Surface tension (liquid - gas) (dyn/cm);

 V_m : maximum Volume of the particle (liquid volume to move) (Cm³);

 ρ_s : particle Density (g/cm³);

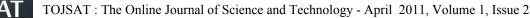
- γ_c : Acceleration (cm/s²);
- θ : The contact angle (degree).

During flotation we have: $F_f = Fc$

$$P_m \cdot \gamma_{\rm lg} \cdot \sin \theta = \rho_s \cdot V_m \cdot \gamma_c \tag{3}$$

Let 's consider the cubic particle: $V_{\text{max}} = d_{\text{max}}^3$ and $P_m = 4d_m$

$$d_{m} = \sqrt[3]{\frac{4\gamma_{\text{lg}}\sin\theta}{\rho_{s}\gamma_{c}}} \tag{4}$$



The calculation of maximum diameter D_m introduced the concept of proportionality factor K (K < 1):

$$d_m = \sqrt[3]{\frac{4k\gamma_{\rm lg}\sin\theta}{\rho_s\,\gamma_c}} \tag{5}$$

Dimension of the air bubble necessary to flotation:

The critical diameter of the air bubble is given by the following relation:

$$D_{critique} = \frac{6 \cdot \alpha \cdot d \cdot \rho_s}{\rho_l} \tag{6}$$

 α : Coefficient of mineralization of the air bubble characterizing the relation of the section of the surface of the mineral air bubble charged with particles (0.03-0.3).

 ρ_s : mineral particles Density (=3.5-17.5g/cm³);

 ρ_l : pulp Density (g/cm³);

d: the diameter (mm).

Methods and Characterization of Minerals:

Sphalerite (ZnS):

System: cubic Density: d=3.5-4.2 Properties: fairly lasts, heavy, very fragile Cleavage: perfect (12faces) Colors: yellow with brown reddish Glare: hard or resinous Transparency: transparency with translucent Use: principal mineral of zinc. Galena (PbS): System: cubic Density: d=7.5-7.6 Properties: to tend, very door Cleavage: very perfect Colors: lead gray Glare: metal sharp



Transparency: opaque

Use: principal lead ores.

Pyrite (FeS₂):

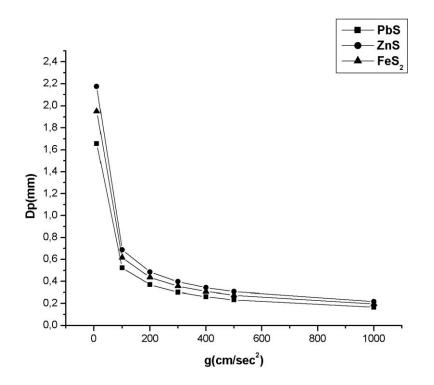
System: cubic Density: d=5-5.2 Properties: last, very heavy, very fragile Cleavage: not Colors: yellow brass blade Glare: metal very sharp Transparency: opaque Use: sulphuric acid. [5-11]

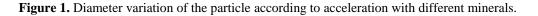
Flotation Study Calculation of the parameters influencing the sulfides flotation:

1. Acceleration Influences:

To carry out the reactions in heterogeneous medium require usually a device of agitation (according to the equation (5)). Its aime is to ensure the best possible contact between the components of a mixture and, if required, to regularize the temperature.

- the case of three minerals:





The figure (1) shows the particle diameter variation according to acceleration with

various minerals and it is noticed that the increase in acceleration supports the reduction in the flotable maximum galenite diameter, the sphalerite and the pyrite.

- For the galena (PbS): $g = 400 \text{ cm/sec}^2$; $D_m = 0.4103 \text{ mm}$.
- For the sphalerite (ZnS): $g = 400 \text{ cm/sec}^2$; $D_m = 0.4909 \text{ mm}$.
- For the pyrite (FeS₂): $g = 400 \text{ cm/sec}^2$; $D_m = 0.4564 \text{ mm}$.

2. Contact angle Influences:

The diameter of the air bubble plays a very important part in the limitation of the contact angle, we note that the contact angle decreases considerably with the reduction of the contacts surface diameter of air bubble.

- The case of three minerals:

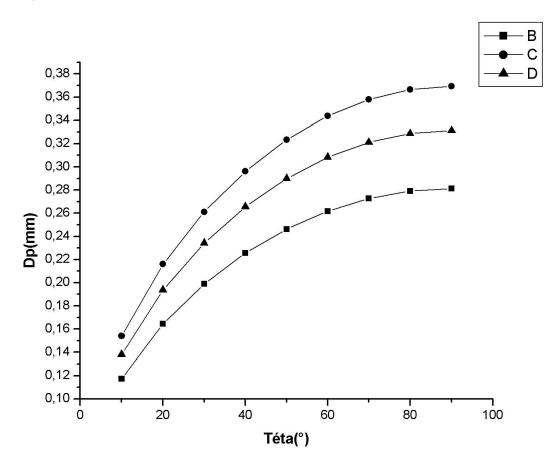


Figure 2. Particle diameter variation according to the contact angle to different minerals.

According to the figure (2) we can note that the increase in the contact angle teta supports the increase in the maximum flotable diameter for the three minerals, sphalerite and the pyrite with g=400 cm/sec².

The calculation results show that:

- For galena (PbS): teta = 40° ; D_m = 0.3705mm.
- For the sphalerite (ZnS): teta =40°; $D_m = 0.4443$ mm.
- For the pyrite (FeS₂): teta = 40° ; D_m = 0.4132mm.

Under the industrial conditions; the time of contacts between the air bubbles and the solid is relatively short for the turbulent mode $(10^{-3}sec)$; what supposes a minimum with the value of the angle contact necessary to preserve favorable kinetics of flotation (we take the contact angle between 30° and 40°). [12-17]

3. Density Influence on the air bubbles diameter:

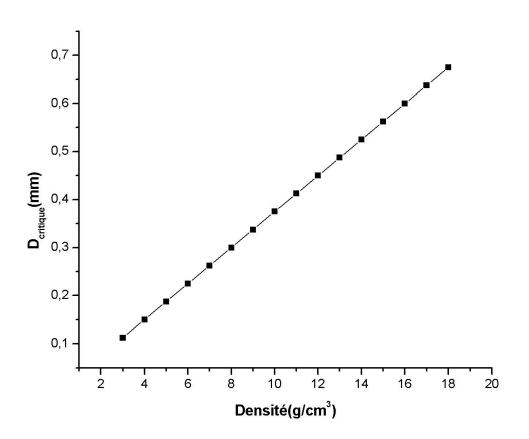
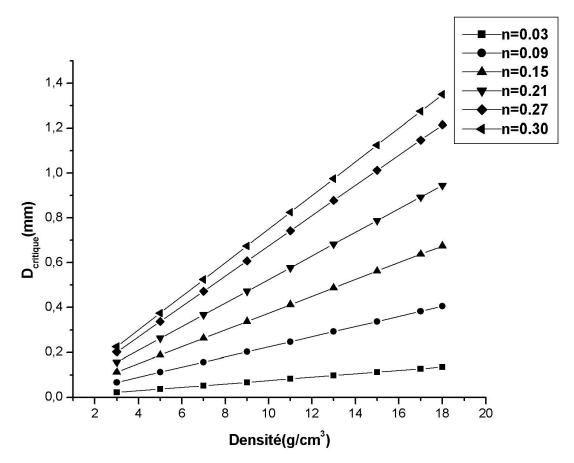


Figure 3. Variation of the critical air bubble diameter according to the density.

Figure (3) shows variation of the critical diameter of the air bubble according to the density of various minerals, and we can note that the diameter of the air bubble increases according to the density.



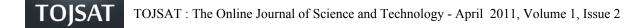
4. Density Influence on the air bubbles diameter with different mineralization coefficients:

Figure 4. Variation of the critical air bubble diameter according to the density with different mineralization coefficients.

Figure (4) shows variation of the critical diameter of the air bubble according to the density with different mineralization coefficients, and we can notice that the increase in the mineralization coefficients supports the increase in the air bubble diameter and the density.

The calculation results show that the minimal critical diameter of the air bubble should not be lower a:

- 0.2000 mm for the flotation of PbS to a maximum diameter of 0.3705 mm
- 0.1530 mm for the flotation of ZnS to a maximum diameter of 0.4443 mm
- 0.1910 mm for the flotation of FeS₂ to a maximum diameter of 0.4132 mm



5. Maximum size of various galenite particles (PbS):

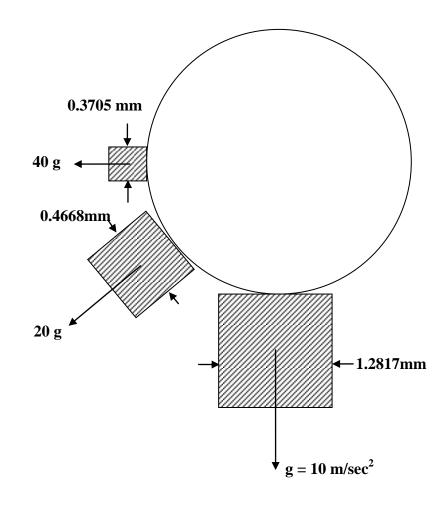


Figure 5. Maximum size of various galenite particles.



6. Maximum size of various sphalerite particles (ZnS):

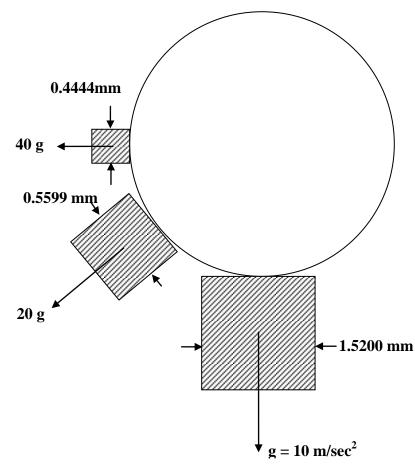


Figure 6. Maximum size of various sphalerite particles.



7. Maximum size of various pyrite particles (FeS₂):

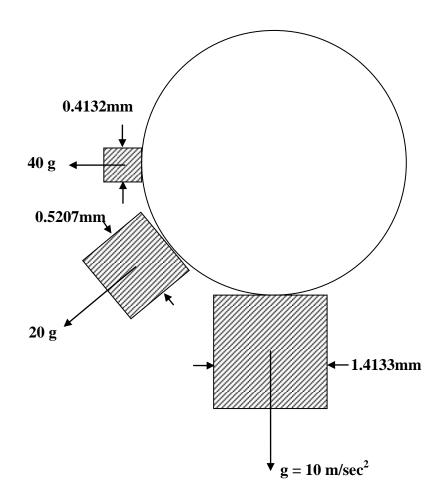


Figure 7. Maximum Dimension of various pyrite particules.

According to figures (5), (6) and (7) it is noted that the increase in acceleration causes the maximum reduction in the diameter of the various flotable mineral particles on bubbles identical (even dimension) under different flow condition ; under all the conditions the maximum size of the particles inversely proportional to the density of floted mineral.

The results of calculates show:

- For galenite (PbS): teta =40°; Dm=0.3705mm.
- For the sphalerite (ZnS): teta = 40° ; Dm=0.4443mm.
- For the pyrite (FeS₂): teta =40°; Dm=0.4132mm. [18-21]



Physicochemical modeling of the pH pulp action on the xanthate concentration necessary in sulphuretted minerals flotation:

The regulation of the pulp pH is one of the essential selectivity parameters of the process of extraction by flotation of the polymetallic ores. The value of the xanthate concentration necessary is important for the regulation of the flotation process and also for the development and the adjustment of a regulation automatic system of the reagent consumption.

Table 1. Concentrations values of ion xanthates in solution necessary to the appearance of lead xanthate on the galenite surface.

pН	Ethyl x	Ethyl xanthate		Isopropyl xanthate		Butyl xanthate	
	mol/l	mg/l	mol/l	mg/l	mol/l	mg/l	
7	1,4.10-6	0,2	<i>4,3.10</i> ⁻⁷	0,06	1,2.10-7	0,02	
8	4,5.10-6	0,5	1,4.10-6	0,2	4,0.10-7	0,06	
9	1,4.10-5	1,7	4,3.10-6	0,6	1,2.10-6	0,2	
10	<i>9,5.10⁻⁵</i>	11,5	2,9.10-5	3,9	8,5.10-6	1,3	
11	3,2.10-4	38.6	<i>9,8.10⁻⁵</i>	13,2	2,9.10-5	4,3	
12	1,5.10-3	181,0	4,6.10-4	62,0	1,3.10-4	19,3	

Calculation is made on the basis of solubility of ethyl xanthate of K lead equalizes to 1, 7.10^{-7} , isopropyl xanthate equalizes to 1, 58.10^{-18} , on the other hand the butylic xanthate of lead equalizes to 1, 35.10^{-19} .

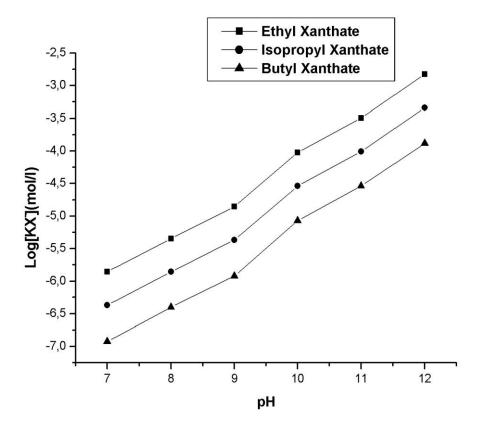


Figure 8. pH variation according to different xanthate types.

Flotation and repair mode of sulphuretted minerals:

The selective flotation of sulphuretted lead minerals starting from the sulphuretted and mixed ores lead-zinc (Zavar Factory in India, Boubekkeur in Morocco, Bouguerou in Italy, Almaliskaya in Russia) with use in quality of depressing for sulfides of zinc and iron: the cyanide (2-100gr/tonne) and the zinc sulfate $ZnSO_4$ (30-700gr/tonne) in the mode cheridane.

At the time of the existence in the sphalerite and pyrite ore of with a weak activity with respect to flotation (Factory Broken Hill), it is necessary to introduce into the floatation cycle of zinc sulfate or a small quantity of cyanide, soda is to float the lead minerals with low fuel consumption of flotation reagent. The suppression of the natural buoyancy of zinc at the time of the cycle of lead-zinc flotation can be reached by addition of a mixture of cyanide and ferrous sulfate. [22]

In the majority of the cases the lead flotation is carried out in medium slightly basic (optimum condition for buoyancy suppression of zinc and iron per cyanide); pH=7-9, creates by soda (100-300gr/tonne), to exclude the suppression from galenite flotation on oxidized surface.

The addition of collector in the crushers supports the buoyancy activation of the galenite and decreases the sphalerite buoyancy.

For the process optimization can be used the automation system illustrated on shape:

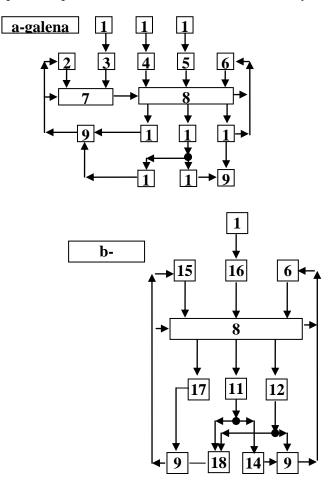


Figure 9. Autoimmunisation systems control and regulation of reagents consummation in the flotation.



- 1- Detector;
- 2- Sodium sulfide batcher;
- 3- Sodium sulphite batcher;
- 4- Zinc sulfate batcher;
- 5- Sulfate batcher of ammonia;
- 6- Xanthate batcher;
- 7- Crushing;
- 8- Flotation;
- 9- Regulation;
- 10- Detector or sensor of concentration of the sulphuretted ions;
- 11- Sensor of pH;
- 12- Sensor of concentration of ions KX-;
- 13- Building block working with the function:
- 14- Building block working with the function:
- 15- Lime dosage;
- 16- Temperature regulator;
- 17- Sensor of concentration of the calcium ions;
- 18- Building block working with the function:

The use of cyanide and zinc sulfate in ore enriching is not in favor of a sufficient selectivity and at the termination end of the lead floatation operation, an activity of sphalerite flotation is noticed. The researchers [40] deduce that most stable zinc sulfide depression is reached by sodium sulfide addition with sodium sulphite in the crushing or flotation cycle. [23-26]

Conclusion

The results of calculate of the physicochemical parameters influence on the sulfides flotation:

- 1- acceleration Influence (g = 400 cm/sec2):
 - D_m (PbS) =0.2628 mm
 - D_m (FeS₂) =0.3083 mm
 - D_m (ZnS) =0.3439 mm.
- 2- contact angle Influence (teta = 40°):
 - D_m (PbS) =0.2255 mm
 - D_m (FeS₂) =0.2656 mm
 - $D_m(ZnS) = 0.2962 \text{ mm.}$

Under the industrial conditions, the particle - bubble contact time is relatively short for the turbulent mode (10^{-3} dryness).

- 3- density Influence on the critical diameter of the air bubbles (N = 0.15):
- 0.2000 mm for the flotation of PbS to a maximum diameter of 0.2255 mm
- 0.1910 mm for the flotation of FeS_2 to a maximum diameter of 0.2656 mm
- 0.1530 mm for the flotation of ZnS to a maximum diameter of 0.2962 mm

- 4- The addition of foaming on the other hand causes the reduction of the rise speed of the air bubbles in pure water the speed of rise increases abruptly.
- 5- Xanthate concentration necessary for the galenite flotation:
 - equalize at least necessary [KX⁻], guaranteeing the appearance of lead xanthate on the galenite surface for a given value of pH;
 - it is the same one for galenite of the various layers;
 - can be calculated for each value of pH according to the equation (4) or (5). •

On the technological level the elimination of salts and shlamms up to 6% supports the stabilization of the enrichment operations succession with reduction in the concentration of reagents, increase in the quality of concentrated and of metals extraction degrees.

The choice of the flotation diagrams of the oxidized and mixed ores lead-zinc depends on the report/ratio and the ores lead-zinc character and the existence of iron sulfide.

Acknowledgement

The authors would like to thank Pr BOUHEGUEL Mustapha, Pr BARKAT Djamel and Dr SLIMANI Rabie for some helpful discussions.

REFERENCES

[1] : AbramovA.A., Ribakov, V.V, Enrichissement des minerais des métaux nobles et rares dans le pays d'asie, d'afrique et d'amerique latine, Moscou ; p.108-140,1991.

[2] : Abramov.A.A, Modélisation physico-chimique des systèmes de flottation; Moscou, p.6-14,1977.

[3] : AbramovA.A., Avdokhin V.M., Oxydation des Minéraux Sulfurés dans les Procédés d'enrichissement, Moscou, "NEDRA", p.161-167, 1989.

[4]: Avdokhin V.M., Oxydation des minéraux Sulfurés dans les procédés d'enrichissement, p. 123-131; 161-167, Moscou, Nedra, 1989.

[5] : Adamov E.B., Evaluation Technologique des ressources Minérales, Méthodes de Recherches, Moscou, p.76-84, 1990.

[6]: Baranov V.F., Guide de Projection des Fabriques d'enrichissement, Tome 1, Moscou, "NEDRA", p.290-293, 1988.

[7] : Bartton,D.H.R;Mc combie;S;W;J.Chem.Soc,Perkin trans I,1975,1574-1585.p.7-9,2002.

[8]: Bogdanov O.S., Maxinov, Théorie et Technologie de Flottation, Moscou, "NEDRA", p.114-116, 1980.

[9]: Cevher Hazrlama El kitab, Editors; Prof.Dr. Guven Anal, Prof.Dr.Gunduz Ateok, June, p.122-125, 1994.

[10] : Choubov L.Y., Ivankov S.I, Réactifs de flottation dans les procédés d'enrichissement des minerais, Tom 1, p.79-91, Moscou "NEDRA",1990.



[11] : Choubov L.Y., Ivankov S.I, Réactifs de flottation dans les procédés d'enrichissement des minerais, Tom 2, p.180-231., Moscou "NEDRA",1990.

[12] : Eren Cancer ORHAN;Sulfide Flotation; Hacettepe Univercity; Ankara;Turkey, p.1-5, 15 October 1997.

[13]: Full public report .Sodium Ethyl Xanthate. Priority exiting chemical N°5.Australian government publishing service .Canberra, p.1-16, May 1995.

[14]:Gaudin. A.M., Flottation, Memorial Volum, p.110-112, New York, 1976.

[15] :Glembotski V.I., Flottation, p.101-110, Mouscou, "NEDRA", 1973.

[16]: Kelly,E.G, Spottiswood,D.J.Introduction to mineral processing, John Wiley and sons,p.75-79, 1982.

[17]: Keller W.D., Rickett E.E., Absorption Of Infred Radiation By Powdred Silicamineral, "Amer-Mineral", p.174,1952.

[18]: Klarck.S, Mémoire des Constantes Physique des Roches, Mir, p.541, 1969.

[19]: Melik.GayKazyan V.I.,Abramov A.A., Méthodes de recherche dans les procédés de flottation, p.128-138, Moscou."NEDRA", 1990.

[20]: Melik.GayKazyan V.I; Bases physicochimique en théorie de flottation. Moscou, p.22-50, 1983.

[21]: Neeraj K.Mendiratta, Kinetic Studies of Sulfide Mineral Oxidation and Xanthate Adsorption ;Blacksburg, Virginia , p.25-28, May 2000.

[22]: NICNAS, Sodium Ethyl Xanthate, Priority Existing Chemical, Secondary Notification Assessment, Report N° 5S,p. 20-22, February 2000.

[23]: Pierre Blazy; El Aid Jdid, Flottation- Mécanismes et Réactifs; Technique d'ingénieur, France, j3350, p.2-7, 1966.

[24]: Pierre Blazy; El Aid Jdid, Flottation- Mécanismes et Réactifs; Technique d'ingénieur, France, j2₂ [j3350, j3360], p.2-17, 1966.

[25]: RaXtchev A.D., Nouvelles méthodes physico-chimiques d'étude des minéraux, p.220-221, Moscou."NEDRA", 1989.

[26]: Sodium Ethyl Xanthate. Chapitre 6, d'autre technique de précipitation .Fin de support 1110-1-4012., p.116-120, 15 Novembre 2001.

[27]: Zongfu D.and John Ralston, Particule-Bubble attachement in mineral flotation ; J.C.I.S, Elsevier Science 217, p.70-76, 1999.