Heat Recovery Technology Applications for the Desulfurization Process of Phosphgypsum

M. Alla[a*], M. L. El Hafyani[a], S. Zouggar[a], E. K. Gharibi[b]

[a]*Laboratory of Electrical Engineering and Maintenance, Higher School of Technology,*
University Mohammed First Oujda, Morocco
[b] *Laboratory of Solid Minerals and Analytical Chemistry, Faculty of Sciences,*
Mohammed First University, Oujda, Morocco

Keywords: ORC, Phosphogypsum, desulfurization, SO2, waste heat, Enthalpy H.

Abstract: The Organic Rankine Cycle (ORC) is a very important technology for converting the deadly heat from which it   is desired to produce mechanical power at low or medium temperatures to produce electricity. This paper presents existing applications and of desulfurization of phosphogypsum (PG). Provided the interest to recover waste heat rejected by thermal devices and industrial processes continue to grow, and favorable legislative conditions are adopted, waste heat recovery organic Rankine cycle systems in the near future will experience a rapid growth at very low temperature. In this study the energy released by the phosphogypsum desulfurization system on the ORC machine will be applied to produce the electricity.

1   INTRODUCTION

As the human population grows, it becomes increasingly dependent on energy; the increasing consumption of fossil fuels has led to more and more environmental problems such as global warming, ozone depletion and atmospheric pollution. Furthermore, along with the fast development of industry, energy shortages and blackouts have appeared more and more frequently all over the world. Due to all these reasons, utilizing low-grade waste heat for energy production has attracted more and more attention for its potential in reducing the fossil fuel consumption. Thus, an excess of heat is generated during many stages of the production and processing of an energy intensive system. Thus, the development of cogeneration capable of recovering and converting and fatal heat into electrical energy, this technology is one of the main pathways to a high-efficiency, low-temperature energy future.

These technologies have been known for the production of electricity, applied in many forms ranging from domestic applications to industrial applications in order to combine heat and electricity, including various Stirling, thermoacoustic and thermofluidic heat engines.

For a very important efficiency, it is necessary that the heat occurs at the lowest possible temperature. This is best achieved by generating energy in combined cycle mode. Commercial combined cycles generally use a gas turbine. These heavy-duty gas turbines with higher output temperatures, and also are technically and economically viable for combined cycle applications. There are five main focus points when optimizing an ORC: the heat source type, the selection of the working fluid, the hardware components, the control strategy and the component layout and sizing. The heat source can be waste heat, solar energy, geothermal heat or biomass combustion.

1.1   Organic Rankine Cycle Applications

1.1.1 Binary Geothermal Power Plants

Geothermal energy refers to both the science that studies the internal thermal phenomena of the terrestrial globe and the technology that aims to exploit it. By extension, geothermal energy also

sometimes refers to geothermal energy from the energy of the Earth that is converted into heat.

To capture geothermal energy, a fluid is circulated in the depths of the Earth. This fluid can be that of a natural captive hot water sheet, or water injected under pressure to fracture a hot and impervious rock. In both cases, the fluid warms up and goes back loaded with calories (thermal energy). These calories are used directly or partially converted into electricity, allowing some locations to be more suitable for geothermal applications than others represent by figure 1:
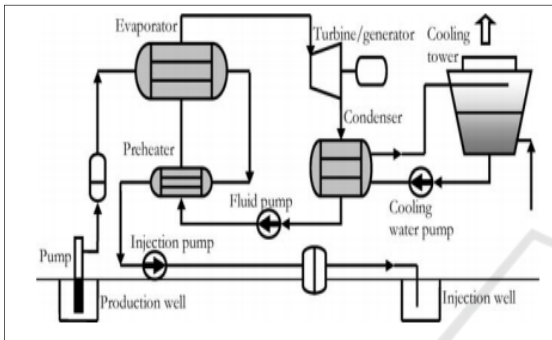

Figure 1: Flow diagram for a binary geothermal power plant.

1.1.2 Solar Thermal Power Systems

Several factors increase the market potential of power plants: the need for distributed power systems in remote areas, the need for sustainable power for the economic growth of developing countries and also for producing clean electricity with the help of renewable energy sources. Rankine cycle modular organic solar power plants operate on the same principle as conventional systems but use an organic fluid instead of steam. The advantages of these systems are as follows:

- Low temperature operation (<300 ° C): low temperature solar collectors and ORC modules that can work well in regions of low solar radiation intensity, such as sub-Saharan regions African.
- Modularity: it is possible to build large solar ORC plants of several MW of power by combining on the same site a large number of ORC modules. Compressed air diaphragm pump and a radial flow.
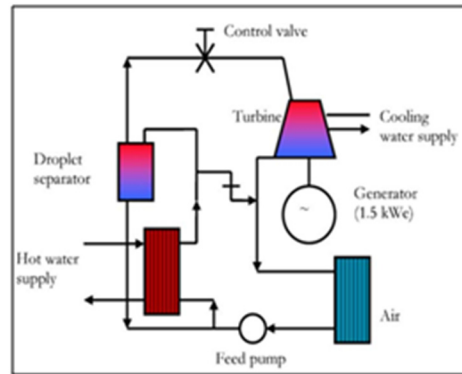- Turbine (65.000 rpm) coupled to a high speed alternator (Fig. 2).

Figure 2: A micro-organic Rankine power system

1.2 Organic Rankine Cycles (ORCs) in Waste Heat Recovery Application

Waste heat is the unused heat generated during a combustion process or any other chemical reaction/thermal process and, then directly exhausted to the environment. Industrial energy intensive processes as well as thermal engines and mechanical equipment's produce large amounts of such waste heat . Exhausts discharged do not only contain high exergy value but also large quantities of pollutants: carbon dioxide (CO_2), nitrogen oxides (NO) and surlphur oxides (SO_x) responsible of high level concentration of atmospheric greenhouse gases and of the global warming. Some developed countries in view of cutting off their harmful gas emissions while decreasing their energy imports in the meantime have evaluated their waste heat recovery potential. A study conducted within the eight largest manufacturing sectors in Canada showed up to 70% energy input lost . According to a report published by the US Department of Energy (DOE) in 2008, the industrial sector alone accounts for about one third of the total energy consumed in the country and contributes in the same proportion to greenhouse gas emissions.
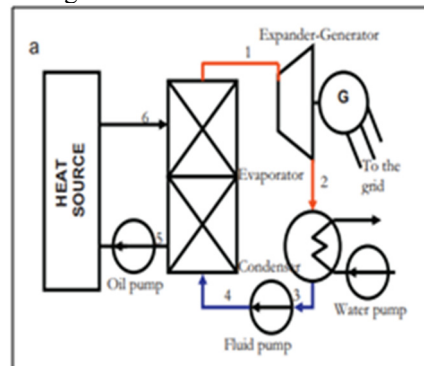

Figure 3: Flow diagram for a waste heat

2 DESULFURIZATION PROCESS OF PHOSPHOGYPSUM

The development of the fertilizer industry leads to the production of more and more phosphoric acid (more than 93% is $CaSO_4.2H_2O$) by treating natural phosphates with sulfuric acid, this industry releases significant amounts of phosphogypsum (PG), Solid phosphogypsum waste often contains substances that are directly hazardous or may become hazardous during storage. Large quantities are produced world-wide and it is estimated that by the year 2000 up to 280 million tones will be produced annually (in Morocco 8 million tons per year).

2.1 Experimental Procedure

Phosphogypsum (PG) is placed in a reaction chamber, attacked with concentrated hydrochloric acid at boiling temperature. Varying amounts of metallic iron are added to the phosphogypsum prior to the etching step. After having dissolved almost all the solid, we filtered cold and kept both the insoluble residue and the solution. The gas released from the reaction chamber is bubbled through solutions that retain the Sulphur dioxide (SO_2) gas. The phosphogypsum reacts in the hydrochloric medium in the presence of iron and the product formed is SO_2 gas can be presented by the following reaction [8]:

$CaSO_4. 2H_2O + 4HCl + Fe \rightarrow Ca^{2+} + 4Cl^- + Fe^{+2} + 4H_2O + SO_2 (g)$ (Reaction 1)
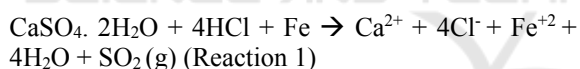
Amounts of 400 g of the raw PG are placed in a reaction chamber, attacked with concentrated hydrochloric acid under boiling temperature. Variable amounts of the metallic iron are added to the PG before the attack step. After dissolving nearly all of solid, we filtered out cold and we kept both the insoluble residue and solution. After, the attack solution was analyzed and the escaped gas was recovered and assayed. The analytical techniques used are X-ray diffraction 6000 SHIMADZU to characterize structure of initial and solid residues after attack. The PG decomposition with a strong HCl acid (varying acid / solid / metal ratios) at the boiling point is carried out in a reaction chamber partially insulated from atmospheric pressure. The gas released from the reaction chamber is bubbled through solutions that keep SO_2 in the form of gas. SO2 gas which is released from the reaction chamber by bubbling into a solution of H_2O_2. Titration of excess H_2O_2 by a strong oxidant, $KMnO_4$, indirectly gives the amount of SO_2 released.

The table 1 gives the values of the thermodynamic quantities calculated in function of the temperature.

The evolution of the enthalpy in function of the temperature is given by the figure 4.
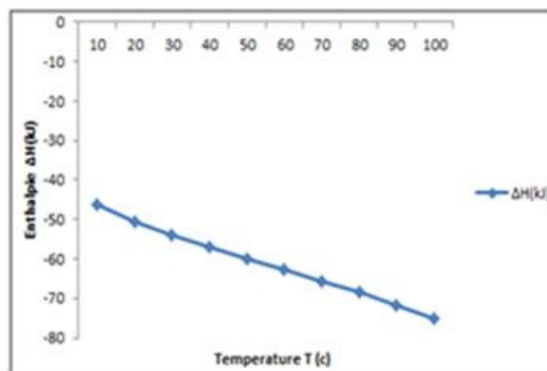

Figure 4: Enthalpies of reaction 1 calculated at different temperatures

Table 1: Thermodynamic parameters of Reaction 1

T (°C)	ΔH (kJ)	ΔS (J/K)	ΔG (kJ)	Log K
10	-46.225	166.395	-93.340	17.221
20	-50.587	151.244	-94.924	16.915
30	-54.041	139.654	-96.377	16.608
40	-57.069	129.822	-97.723	16.302
50	-59.944	120.786	-98.976	16.000
60	-62.752	112.228	-100.140	15.702
70	-65.579	103.867	-101.221	15.409
80	-68.546	95.347	-102.217	15.120
90	-71.708	86.519	-103.127	14.835
100	-75.129	77.227	-103.946	14.552

As shown as in Fig. 1 Enthalpy increases linearly as a function of temperature, which implies that our system of desulfurization of phosphogypsum is exothermic, which requires the valorization of this fatal thermal energy to protect the environment.

2.2 Mathematical Model

Energy and energy analyzes based on the first and second laws of thermodynamics are evaluated for

different organic working fluids under different working conditions.

For the sake of simplicity, the internal irreversibility and the pressure drops in the evaporator, the estimation of the thermodynamic properties of the condenser and the pipes will be neglected. And each component is considered a constant and stable flow system. Introduce the equations to perform the thermodynamic comparative analysis.

Evaporator/Vapor Generator

$$\Delta S = \Delta Q/T \qquad (1)$$
$$Q = m \cdot (h_{in}t - h_{out}) \qquad (2)$$

Turbine

$$W = m_r \cdot (h_{int} - h_g) \qquad (3)$$
$$V_{int} = m_r * v_{int} \qquad (4)$$
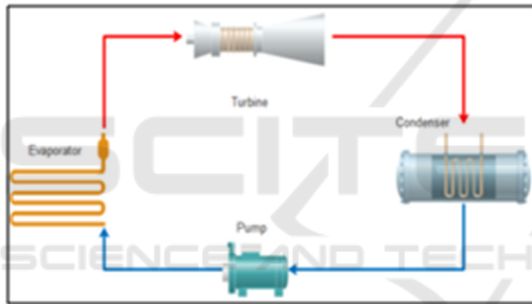$$V_{out} = m_r * v_{out} \qquad (5)$$

Figure 5: Schematic diagram of an ORC system

2.3 Choice of the Working Fluids

It is clear that, in order to calculate the ORC system performance, a relevant number of parameters are to be set. The inlet temperature of the heat source and sink, the pinch temperature difference and flow rate of the heat source were assumed in Table 2. The flow rate of the heat sink is calculated to fulfill the cooling needs. Saturated vapor was assumed at the turbine inlet in subcritical ORC system. The basic assumptions for the plant components are also listed in Table2.

Table 2: Assumptions for heat source and sink and power plant components.

The temperature of the thermal water, °C	90
The temperature of the cooling water, °C	20
The pinch temperature difference in both heat exchangers, °C	5
The mass flow rate of the geothermal water, kg/s	1
Isentropic efficiencies for the turbine	0.9
Isentropic efficiencies for the pump	0.75
Generator efficiency	0.96
Water pump efficiency	0.75
Turbine outlet quality	0.8

According to the temperature-entropy diagrams, fluids show three different types of slope on their saturation vapor curves and can be categorized into three groups: (1) dry fluids have positive slope, (2) wet fluids have negative slope, (3) isentropic fluids have nearly vertical saturated vapor curves. The wet fluids are generally not adequate for subcritical ORC systems because they become saturated once they go through a large enthalpy drop after producing power in the turbine, and the condensate of the fluids imposes a threat of damage to the turbine. The dry and isentropic fluids can prevent the above disadvantage [10]. Table 3 lists some properties of the working fluids considered here.

Table 3: Basic thermodynamic and environmental properties of the selected fluids [10]

|	Substance	Physical data				Safety data	Environmental data			Type
		M	t_{bp}	t_{crit}	P_{crit}	ASHRAE 34 safety group	ALT	ODP	GWP (100 yr)	
1	R123	152.93	27.82	183.68	3.6	B1	1.3	0.02	77	Isen
2	R245ca	134.05	25.13	174.42	3.9	A1	62	0	693	Dry
3	R245fa	134.05	14.9	154.05	3.6	B1	7.6	0	1030	Isen
4	R600	58.12	–0.55	151.98	3.7	A3	0.02	0	~20	Dry
5	R236ea	152.04	6.19	139.29	3.5	n.a.	8	0	710	Dry
6	R600a	58.12	–11.67	134.67	3.6	A3	0.02	0	~20	Dry
7	R236fa	152.04	–1.44	124.92	3.2	A1	240	0	9810	Dry
8	R152a	66.05	–24.02	113.26	4.5	A2	1.4	0	124	Wet
9	R227ea	170.03	–16.45	101.65	2.9	A1	42	0	3220	Dry
10	R134a	102.03	–26.07	101.06	4.0	A1	14	0	1430	Isen
11	R143a	84.04	–47.24	72.71	3.7	A2	52	0	4470	Wet
12	R218	188.02	–36.83	71.95	2.6	A1	2600	0	8830	Isen
13	R125	120.02	–48.09	66.02	3.6	A1	29	0	3500	Wet
14	R41	34.03	–78.12	44.13	5.8	n.a.	2.4	0	92	Wet
15	R170	30.07	–88.60	32.18	4.8	A3	0.21	0	~20	Wet
16	CO_2	44.01	–78.40	30.98	7.3	A1	>50	0	1	Wet
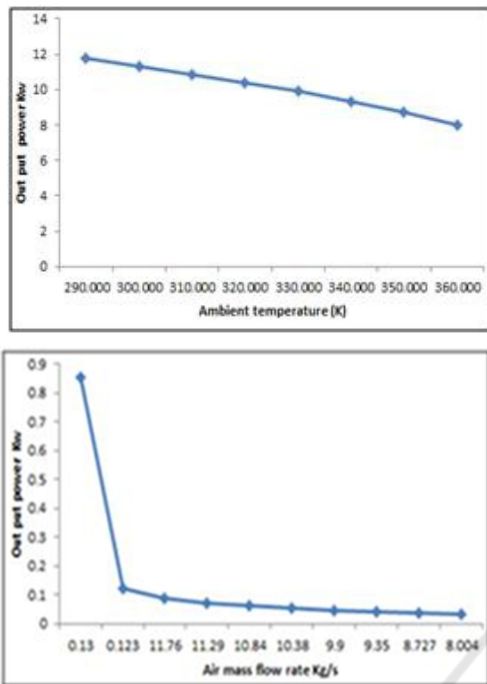
Figure 6: System output net power versus each input
Parameter (a) air mass flow rate (kg/s) and
(b) ambient temperature (K).

As shown as in Fig. 6a and b, the system output net power increases evidently and linearly with the increase of exhaust flow rate and temperature. In other words, using the exhaust heat as much as possible and the higher grade of heat source will improve the system output net power according to the calculations obtained, the energy produced by the desulphurization system of phosphogypsum (PG); the energy released by waste heat is 0.2 Mw < waste heat < 200Mw so we apply our system to the Rankine cycle.

3 CONCLUSION

The storage and management of a huge amount of PG presents a serious problem on the environment, so the objective of this work is to valorize the thermal energy released by the desulfurization system of the PG to produce electricity by applying the cycle from Rankine.

REFERENCES

M. Canut, Belo Horizonte, Universidade Federal de Minas Gerais, 2006.

C. A. Gregory, D. Saylak. W. B. Ledbetter, TRR Journal, 998, pp 47-52 (1984).

Bartow, FIPR Publication, 01, pp 124-119 (1996).

P. R Ernani, M. S. Ribeiro, C. Bayer, Sci. Agric., 58:825-831, 2001.

P. A. Bellingieri, E.G. Bertin, L. Z. Mays, Científica, 31 pp 81- 89 (2003).

P. Bhawan, E.A. Nagar - Delhi: Central Pollution Control Board, 2012.

G.A. Fattah, M.S. Altouq, A.A. Shamsaldien, Life Sci., 13(3) (2016) 65-78.

S. Oumnih, E. K. Gharibi, E. B. Yousfi, N. Bekkouch, K. El Hammouti, JMES, 2017 Volume 8, Issue 1, Page 338-344.

Chen H et al. A review of thermodynamic cycles and working fluids for the conversion of low-grade heat. Renew Sustain Energy Rev 2010. doi:10.1016/j.rser.2010.07.00

Calm JM, Hourahan GC. Refrigerant data summary. Eng Syst 2001;18(11):74–88.

Badr O, O'Callaghan PW, et al. Performances of Rankine cycle engines as functions of their expanders' efficiencies. Appl Energ 1984;18(1):15–27.

Badr O, O'Callaghan PW, et al. Rankine cycle systems for harnessing power from low-grade energy sources. Appl Energ 1990;36:263–92.

Lee KM, Kuo SF, Chien ML, et al. Parameters analysis on organic Rankine cycle energy recovery system. Energ Convers Manage 1988;28(2):129–36.

Lee MJ, Tien DL, Shao CT. Thermophysical capability of ozone-safe working fluids for an organic Rankine cycle system. Heat Recov Syst CHP 1993;13(7):409–18.

Hung Tzu-Chen. Waste heat recovery of organic Rankine cycle using dry fluids. Energ Convers Manage 2001;42:539–53.

Hung TC, Shai TY, Wang SK. A review of organic Rankine cycles (ORCs) for the recovery of low-grade waste heat. Energy 1997;22(7):661–7.

Liu BT, Chien KH, Wang CC. Effect of working fluids on organic Rankine cycle for waste heat recovery. Energy 2004;29:1207–17.

Kribus A, Zaibel R, Carey D, et al. A solar-driven combined cycle power plant. Sol Energy 1998;62(2):121–9.

Angelino G, Invernizzi C. Cyclic methylsiloxanes as working fluids for space power cycles. J Sol Energ Eng 1993;115:130–7.

Moustafa S, Hoefler W, El-Mansy H, et al. Deign specifications and application of a 100 kWth cogeneration solar power plant. Sol Energy 1984;32(2):263–9.

Gianfranco Angelino, Piero Colonna di Paliano. Organic Rankine cycles (ORCs) for energy recovery from molten carbonate fuel cells. American Institute of Aeronautics and Astronautics; 2000. p. 2–11.

Ingwald Obernberger, Peter Thonhofer, Erwin Reisenhofer. Description and evaluation of the new 1000 kWel organic Rankine cycle process integrated

in the biomass CHP plant in Lienz, Austria. Euroheat Power 2002;10:1–17.

Weidao Shen, Zimin Jiang, Jungeng Tong. Thermodynamics engineering. 3rd ed. China: Higher Education Publishing Company; 2000.

Shilie Weng. Combustion turbine. China: Mechanical Industry Publishing Company; 1989.

REFPROP Version 6.01, NIST Standard Reference Database 23, the Secretary of Commerce, America; 1998.

Modelica Association. Specification, Tutorials [EB/OL], http://www.modelica.org/.

Dynasim AB, Dynamic Modeling Laboratory [EB/OL], http://www.dymola.com/.

Tchanche, B.F.; Lambrinos, G.; Frangoudakis, A.; Papadakis, G. Low-grade heat conversion into power usingorganic Rankine cycles – A review of various applications. Renew. Sustain. Energy Rev. 2011, 15, 3963–3679. [CrossRef]

Bronicki, L. Short review of the long history of ORC power systems. In Proceedings of the ORC2013, Rotterdam, The Netherlands, 7–8 October 2013

Crook, A.W. Profiting from Low-Grade Heat; Institution of Electrical Engineers: Stevenage, Hertfordshire, 1994.

Siemens. Fact Sheet: Organic Rankine Cycle. Available online: http://www.energy.siemens.com/nl/pool/hq/power-generation/steam-turbines/orc technology/Siemens_FactSheet-ORC-Module.pdf (accessed on 1 May 2016).

Turboden. Organic Rankine Cycle Technology. Available online: http://www.turboden.eu/en/public/downloads/200-300%20kW.pdf (accessed on 5 April 2016).

Uusitalo, A.; Honkatukia, J.; Backman, J.; Nyyssönen, S. Experimental study on charge air heat utilization of large-scale reciprocating engines by means of organic Rankine cycle. Appl. Therm. Eng. 2015, 89, 209–219. [CrossRef]

MIROM. Verbrandingsinstallatie: enkele cijfers. Available online: http://www.mirom.be/verbranding_cijfers.html (accessed on 1 May 2017).

David, G.; Michel, F.; Sanchez, L. Waste Heat Recovery Projects Using Organic Rankine Cycle Technology—Examples of Biogas Engines and Steel Mills Applications; World Engineers Convention: Geneva, Switzerland, 2011.

Fernández, F.J.; Prieto, M.M.; Suárez, I. Thermodynamic analysis of high-temperature regenerative organic Rankine cycles using siloxanes as working fluids. Energy 2011, 36, 5239–5249. [CrossRef]

Bao, J.; Zhao, L. A review of working fluid and expander selections for organic Rankine cycle. Renew. Sustain. Energy Rev. 2013, 24, 325–342. [CrossRef]

Stijepovica, M.Z.; Linke, P.; Papadopoulos, A.I.; Grujic, A.S. On the role of working fluid properties in Organic Rankine Cycle performance. Appl. Therm. Eng. 2012, 36, 406–413. [CrossRef]

Maraver, D.; Royo, J.; Lemort, V.; Quoilin, S. Systematic optimization of subcritical and transcritical organic Rankine cycles (ORCs) constrained by technical parameters in multiple applications. Appl. Energy 2014, 117, 11–29. [CrossRef]

Lecompte, S.; Huisseune, H.; van den Broek, M.; De Paepe, M. Methodical thermodynamic analysis and regression models of organic Rankine cycle architectures for waste heat recovery. Energy 2016, 87, 60–76. [CrossRef]

Bell, I.H.; Wronski, J.; Quoilin, S.; Lemort, V. Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermophysical property library CoolProp. Ind. Eng. Chem. Res. 2014, 53, 2498–2508. [CrossRef] [PubMed]

Pacheco, J.E.; Showalter, S.K.; Kolb, W.J. Development of a molten-salt thermocline thermal storage system for parabolic trough plants. J. Sol. Energy Eng. 2002, 124, 153–159. [CrossRef]

Gamal A., Majida Sultan A. et AltafAbdulla S.,Life Sci., 13(3) (2016) 65-78,

SfarFelfoul H., Clastres P. , Ben Ouezdou M., Carles-Gibergues A. Proceedings of InternationalSymposium on Environmental Pollution Control and Waste Management 7-10 January 2002, Tunis (EPCOWM (2002) 510-520.

Seidel G., Huckauf H., Starck J., Kerchove P. and Chassard A., Technologie des ciments, chaux, plâtre Ed. SEPTIMAZ-Paris, (1980)

Azimi G., Papangelakis V.G. and Dutrizac J.E., Fluid. Phase Equilibr., 260 (2007) 300–315;

Daligand, Daniel. Plâtre. Ed. Techniques Ingénieur, (2002).

Cooper J., Lombardi R., Boardman D. and Carliell-Marquet C., Resour. Conserv. Recy.,57 (2011) 78–86,

Walan P., Davidsson S., Johansson S., Höök M., Resour. Conserv. Recy.,93 (2014) 178–187,

Tayibi H, Choura M , A. Lopez F., J. Alguacil F., Lopez-Delgado A., J. Environ. Manage., 90 (2009) 2377–2386,

Becker, P. (1989). Phosphates and phosphoric acid: raw materials, technology, and economics of the wet process. Revised and expanded (Vol. 6). Marcel Dekker, Inc. ISBN :0824779762.

El Cadi A., Fakih Lanjri A., Lalilti A., Chouaibi N., Asskali A., Khaddor M.,J. Mater. Environ. Sci. 5 (S1) (2014) 2223-2229, ISSN: 2028-2508,

Aliedeh M. A., and Jarrah A. N., Sixth Jordanian International Chemical Engineering Conference, Amman, Jordan (2012),

Hou Y., MA L., Zhang J. and Ning P.,Journal of Kunming University of Science and Technology, 35(3), (2010),

Zhu Miao, Hairui Yang, Yuxin Wu, Hai Zhang, and Xuyi Zhang., Ind. Eng. Chem. Res., 51(15) (2012) 5419-5423,

Guidelines for Management and Handling of Phosphogypsum Generated from Phosphoric Acid Plants. Central pollution control board, Delhi India(2014).

Xie L. G., Ma L. P., Dai Q. X., Mao Y. Zhang H, and Ma J.,Adv. Mat. Res.,726-731 (2013) 331-339