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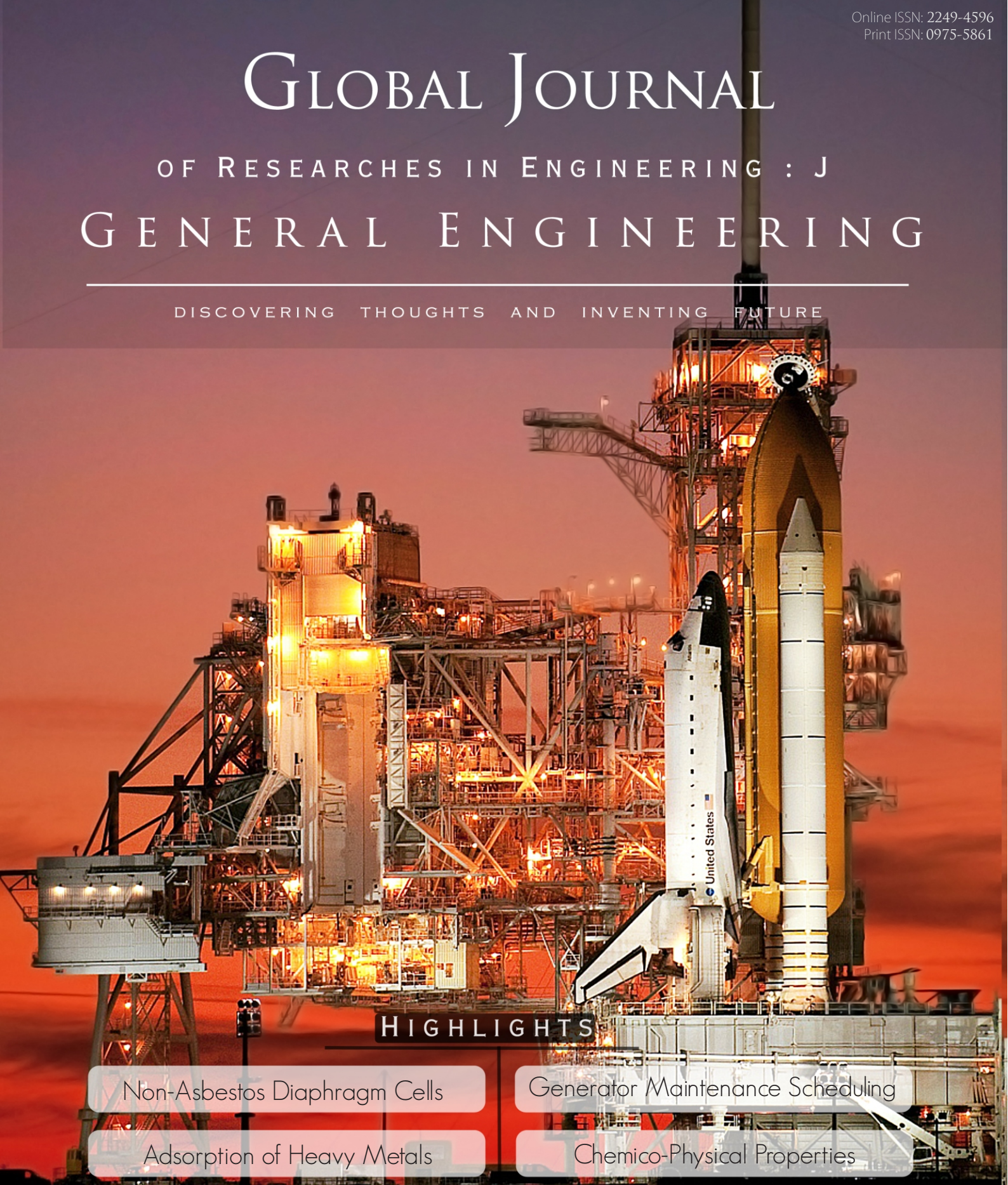

Highlights

- Non-Asbestos Diaphragm Cells
- Generator Maintenance Scheduling
- Adsorption of Heavy Metals
- Chemico-Physical Properties

Atlantis on Launch Pad, NASA

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Operational Simulation of Solar-Powered Non-Asbestos Diaphragm Cells for the Production of Caustic Soda

By Babatope Olufemi , Monisola Omotayo , Oluseyi Olawuwo , Oluwaseun Sese & Moradeyo Odunlami

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Abstract - Mathematical modeling and simulation of an experimental study was performed using an array of solar panels to power three non-asbestos diaphragm type electrochemical cells whose anodes consisted of carbon rods and cathodes made up of stainless steel plate for the electrolysis of a 25 % w/w sodium chloride solution, with the aim of producing caustic soda. The non-asbestos diaphragms served to hinder the formation of unwanted substances as well as permit reasonable production of the desired products. The three non-asbestos diaphragm cells exhibited various characteristic performances, which is a reflection of their design, fabrication, composition, intensity of the sun on any particular day, the length of time the panels were exposed to sunlight and operational parameters. The non-asbestos diaphragm D3 with composition of 60 % w/w Portland cement, 20 % w/w silica and 20 % w/w polyvinyl chloride (PVC) indicated the highest yield of caustic soda per d.c Watt with specific electrical energy supplied. The simulated values predicted the operation closely as the maximum positive and negative deviations of all modeled from experimental values are between +0.07 and – 0.06 respectively. The research served as an encouraging inquisitive foundation into the possibility of producing caustic soda directly from solar powered electrolytic diaphragm cells with the aim of designing better cells as well as investigating key factors that affects cell performance in view of present conventional modes of electrochemical production.

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Keywords : Catholyte, diaphragm, energy, non-asbestos, simulation, solar.

I. Introduction

The chlor-alkali (also called "chlorine-caustic") industry is one of the largest electrochemical technologies in the world. The electrochemical production of caustic soda from brine in the chlor-alkali industry, with chlorine and hydrogen as the by-products is one of the leading industrial production processes in the chemical industry. According to Alkire and Braatz (2004), electrochemical processes provide the only commercially viable means for the production of caustic soda, chlorine and some chemical products. Chlorine and/or caustic soda is involved directly or indirectly in the manufacture of about 70 percent of all chemical products (Ohm, 2007). The threat of inadequate electrical power has resulted in much effort toward reducing electrical power consumption.

The chlor-alkali process is the most economically important electrosynthetic process (Minteer, 2002). It is an energy intensive process and is the second largest consumer of electricity (2400 billion kWh) among electrolytic industries. In 2006, about 84 % of the total world chlorine capacity of about 59 million metric tons was produced electrolytically using diaphragm and membrane cells, while about 13 % was made using mercury cells (Tilak et. al, 2007). The diaphragm cell alone accounted for about 62% production (Tilak et. al, 2007).

According to Ohm (2007), a typical world-scale chloralkali-electrolysis plant produces above 1,000 tons of caustic soda a day. For this it consumes a shipload of salt (about 1,700 tons) and enough electricity to power a town in Germany with 130,000 inhabitants. Power consumption accounts for approximately 60 to 70 % of the total cost of industrial chlor-alkali production (Minteer, 2002; Patel, 2009). In addition, the power supply is highly unreliable, with frequent fluctuations, resulting in lower operational efficiency and higher input cost. Another inputs cost such as gas and petroleum fuel for running the captive power plant are rising steadily and do not show any signs of reduction in the near future. Cheap availability of gas is also a major concern.

Although the process chemistry of the chlor-alkali electrolytic production of caustic soda is simple to understand, the design and operational issues are vastly complex (Gunatillaka and Achwal, 2003). This particular area of production has witnessed, and is still witnessing drastic changes in the methods of production, all of which are directed towards achieving better ways of production in terms of yield, economics, operation, instrumentation, durability, environmental suitability and improvement on equipment design. Recently, low energy consumption in chlor-alkali cells using oxygen reduction electrodes was investigated by Kiros and Bursell (2008). A novel electrolytic cell which reduced power consumption by 91 % was recently developed with significantly superior kinetics, selectivity and efficiency compared to the traditional types of chlor-alkali cells for the production of caustic soda (Minteer,

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2002). The effect of magnetic field in chlor-alkali cells performance was also studied by Minteer and Burney (2005). Performance and durability enh ancement had been investigated for another chlor-alkali cell by Ichinose et *al.* (2004). Application of simulation results as well as relevant parameters and design criteria in the electrochemical industry for the operation of an Expanded Area Diaphragm Cell (EADC) for the electrochemical production of caustic soda with some results similar to what is obtainable in the industry had been carried out (Olufemi, 2008). Mathematical models which are abstract model that uses mathematical language to describe the behavior of a system are useful in electrochemical engineering.

In view of the above concerns, the chlor-alkali sector which is a basic driver of the economy has to play a pro-active role in optimizing energy efficiency and reducing wastage. Among the various strategies aimed to meet energy demand, efficient use of energy and its conservations emerges to be the least cost option in a global competitive environment. In energy conservation conscious countries, Energy Conservation Acts (ECAs) has specified the list of energy intensive industries and establishments as designated consumers. Chlor-alkali is one of such industries. Such consumers will have to carry out certain mandatory functions one of which is implementing techno-economically viable recommendations. The Chlor-Alkali industry has to aggressively pursue this agenda, not for meeting any lofty social obligation, but to ensure its own survival and growth. Members of the Chlor-alkali industry can adopt several such strategies. Reduced energy-consuming chlor-alkali process through solar power derived energy is a good recommendation for the process.

This work is set-out to study and put forward successful implementation of techno-economically viable recommendations in the chlor-alkali industry. The possibility of this is to be explored by theoretical investigation and experimental demonstration of the usage of solar powered electrolytic non-asbestos diaphragm cells for the production of caustic soda, with consideration for their performance and operational characteristics.

II. Experimental

The experimental set up consisted of electrochemical cells with anolyte and catholyte compartments, graphite anodes, stainless steel cathodes, array of solar panels producing electric current, a voltmeter, an ammeter, a charge controller and ducts used to collect products of electrolysis. Additional apparatus employed in the preparation of 25 % w/w brine and 2.78 M HCl for titration were; volumetric flask, a measuring cylinder, an electronic weighing balance, a stirrer, distilled water and crystalline sodium chloride. Apparatus involved in the titration were beakers, retort, burette, conical flask, and pipette. A total of 6 hours electrolysis time was taken for each daily run, with the open and closed cell voltages and current taken at hourly intervals for three days a week. Inlet temperature of brine was 313 K for all runs, while the final is about 315 K for all runs. Non-asbestos plates with compositions given in Table 1, were separately prepared, and were subsequently adhered to the cathode plates, for use as diaphragms. The schematic electrochemical operational diagram for all the cells is shown in Figure 1.

Table 1 : Weight percent of non-asbestos diaphragms

Material	Diaphragm D1	Diaphragm D2	Diaphragm D3
Silica	10%	15%	20%
PVC	10%	15%	20%
Cement	80%	70%	60%

Solar modules were firmly fixed in place, in a manner suitable to withstand all expected loads. The modules were mounted with the orientation and tilt angle required for optimum performance. Its location was selected to have direct access to sunlight from 0900 to 1500 hours GMT. The tilt angle was maintained at 20 degrees to the horizontal, with modules facing south in the northern hemisphere or north in the southern hemisphere as the case may be. During installation of the modules, so as to avoid the destruction of the solar cells, bypass diodes and junction box, the correct polarity was observed and blocking diodes were used to prevent reversal flow of current to the panels. Positive wires from modules were connected to the positive terminal of the charge controller and negative wires from the modules were connected to the negative terminal of the charge controller. Positive wires from the charge controller were connected to the cell anodes and negative wires from the charge controller were connected to the cell cathodes. Insulated copper wires were used to connect the panels in parallel to the charge controller and cells.

The voltage supplies from the panels were suitable to drive the electrochemical reaction and overcome circuit resistances. The theoretical decomposition voltage needed is 2.3 V. The parallel array of the solar panels used has an average open circuit voltage of about 18.4 V. The open circuit voltage was taken at the beginning of each run on a daily basis, and each cell was operated for three days a week for a total of five weeks. The products generated were chlorine gas, hydrogen gas and caustic soda solution. It was observed that after the second day of operation, a sizeable quantity of liquor had been produced and consistent production followed thereafter. Electrolytic product was consequently withdrawn from the cathodic end of the electrolytic cell.

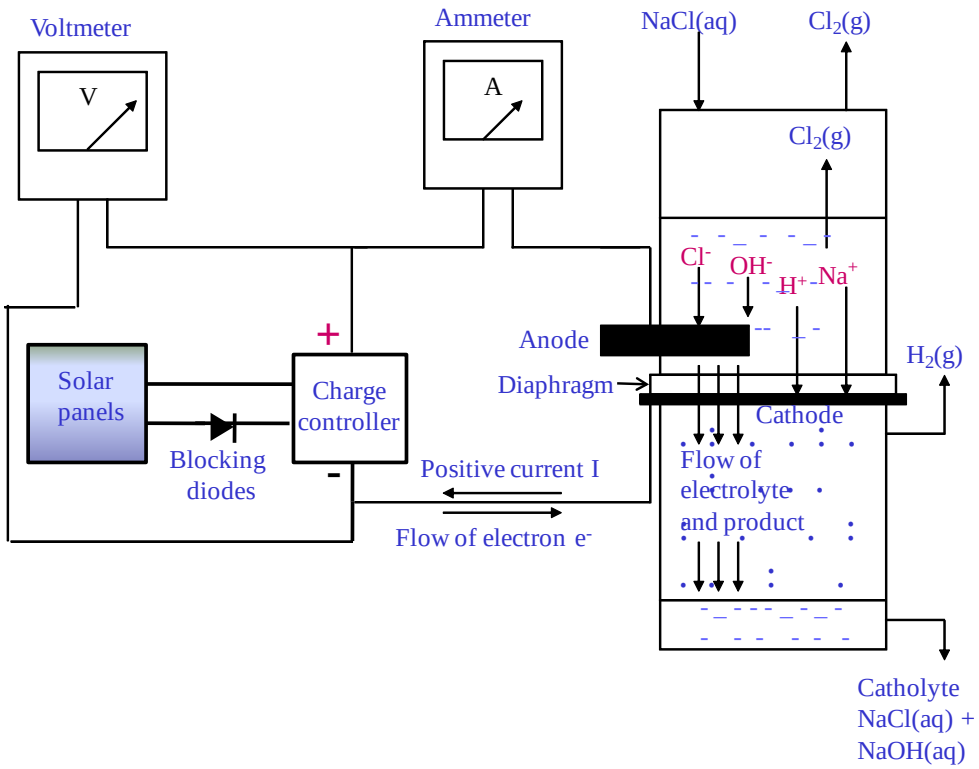

Figure 1 : Schematic electrochemical operational diagram of solar powered diaphragm cells

III. Mathematical Model Development

The overall electrically-driven reaction within the cells is given as:

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH\,(aq) + H_2(g) + Cl_2(g) \quad (1)$$

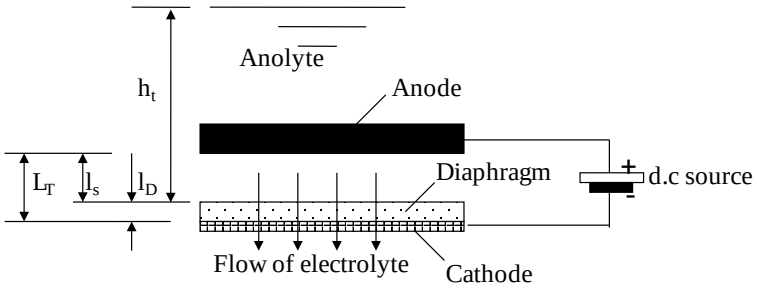

Figure 2 : Spatial arrangement of the anode, diaphragm and cathode

The arrangement of the anode, anolyte height, diaphragm and cathode with the direct current (d.c) source for the cells are shown in Figure 2.

The total cell voltage V must be high enough to drive the electrochemical reaction despite all circuit resistances. Since a dry diaphragm is non-conducting, the performance of the cell depends on the hydrodynamic flow process through the wet porous diaphragm. Fluid flow in porous media is very similar to fluid flow in packed beds, due to the similarity of the flow channels through which fluid passes (Seader and Ernest, 1998). If A_D is the total surface area of the diaphragm normal to the direction of fluid flow, the average velocity across the cross-sectional area of the diaphragm is given as:

$$v_{D,ave} = \frac{\int_0^{A_D} v_{ave}\,dA_D}{\int_0^{A_D} dA_D} = \frac{\pi D_P{}^2 \varepsilon^3 (P_O - P_L)}{144(1-\varepsilon)^2 \tau l_D \mu} \quad (2)$$

and the volumetric flow rate of fluid across the diaphragm surface is given as:

$$\dot{V}_D = \frac{A_D.\pi {D_P}^2 \varepsilon^3 (P_O - P_L)}{144(1-\varepsilon)^2 \tau l_D \mu} \quad (3)$$

If Λ is the equivalent conductance of the flowing electrolyte through the diaphragm, the dynamic resistance of the diaphragm is given as:

$$R_D = \frac{\pi {D_P}^2 \varepsilon^3 (P_O - P_L)}{144\Lambda(1-\varepsilon)^2 \tau \mu} \quad (4)$$

Also, the dynamic resistance of the electrolyte as it flows through the cell is:

$$R_S = \frac{\pi D_p^2 \varepsilon^3 (P_O - P_L) l_S}{144\Lambda(1-\varepsilon)^2 \tau l_D \mu} \quad (5)$$

If the anode overvoltage is η_a, the cathode overvoltage is η_c, the dynamic resistance of the other miscellaneous components in the circuit is R_m, the average modelled current is I_{MD}, then

$$V = 2.3 - \eta_A + \eta_C + \frac{\pi {D_P}^2 \varepsilon^3 (P_O - P_L) l_S I_{MD}}{144\Lambda(1-\varepsilon)^2 \tau l_D \mu} + \frac{\pi {D_P}^2 \varepsilon^3 (P_O - P_L) I_{MD}}{144\Lambda(1-\varepsilon)^2 \tau \mu} + I_{MD} R_m \quad (6)$$

Rearranging Equation (6) and solving for the average current, I_{MD}

$\Rightarrow$

$$I_{MD} = \frac{V - 2.3 + \eta_A - \eta_C}{\left[\frac{\pi D_P^2 \varepsilon^3 (P_O - P_L)}{144\Lambda(1-\varepsilon)^2 \tau \mu}\left(\frac{l_s}{l_D} + 1\right) + R_m\right]} \quad (7)$$

The average electrical power required by the cell is given as:

$$P_{MD} = \frac{V^2 - 2.3V + \eta_A V - \eta_C V}{\left[\frac{\pi D_P^2 \varepsilon^3 (P_O - P_L)}{144\Lambda(1-\varepsilon)^2 \tau \mu}\left(\frac{l_s}{l_D} + 1\right) + R_m\right]} \quad (8)$$

Equation (7) gives the value of the modelled current (I_{MD}) in Amperes, and Equation (8) gives the power requirement of the cell at any time.

The rate of formation of NaOH depends on the influx of Na^+ ions passing through the diaphragm from the anode to the cathode compartment. Due to the similarity of flow channels in the diaphragms, according to Olufemi et *al.* (2000) and Olufemi (2008), the Geometrically Dependent Operational Current Effectiveness (GDOCE) based on cell design geometry and operating condition can be utilized in modeling the cells productivity. The GDOCE is defined as the ratio of the minimum current density required to convert completely the influx of the electrolyte, to the minimum current density furnished by either electrode.

$$\eta_{MD} = \frac{I_{MN} / A_{EL}}{I_{MD} / A_{AC}} \quad (9)$$

If $\eta_{MD} \leq 1$, then

$$(I_{MN} / A_{EL}) \leq (I_{MD} / A_{AC}) \quad (10)$$

If $\eta_{MD} \geq 1$, it means that the efficiency of the cell is not geometrically dependent, and could only be determined through other means. The minimum current required to produce 100 percent of the desired product through the complete conversion of the influx of the electrolyte feed can be obtained as follow:

$$I_{MN} = \frac{N_A z w \rho_{EL} \dot{V}_D}{e_{WE}} \quad (11)$$

A_{EL} is the most geometrically uniform electroactive surface area of the separator for either side of the two half-cells. A_{AC} represents the electroactive surface area of the electrode that has the most geometrically uniform electroactive surface area per unit volume of effective inventory of electrolyte within the reactor (Pletcher and Walsh, 1990).
Thus for the anode,

$$A_{IA} = \frac{A_A}{\dot{V}_D} \quad (12)$$

For the cathode,

$$A_{IC} = \frac{A_C}{\dot{V}_D} \quad (13)$$

The particular electroactive surface area of the electrode that gives the highest value between A_{IA} and A_{IC}, gives the value of the A_{AC} to be used for the determination of the GDOCE.

From the foregoing based on Faradays laws of electrolysis, the maximum electrolytic yield of caustic soda within the cell per unit time is given as:

$$\dot{m}_{HS} = \frac{I_{MD} e_{WS}}{N_A z} = \frac{(V - 2.3 + \eta_A - \eta_C) e_{WS}}{\left[\frac{\pi D_P^2 \varepsilon^3 (P_O - P_L)}{144 \Lambda (1-\varepsilon)^2 \tau \mu} \left(\frac{l_s}{l_D} + 1 \right) + R_m \right] N_A z} \quad (14)$$

where,

$N_A = 6.02205 \text{ X } 10^{26}$ kmol^{-1}, z = 1.60219 X 10^{-19} C,

e_{WS} = 40 kgkmol^{-1}, e_{WE} = 58.5 kgkmol^{-1}

By introducing the GDOCE, which gives the constructive portion of the current density available for the desired reaction, the modelled electrolytic yield of caustic soda within the cell per unit time is given as:

$$\dot{m}_{MS} = \frac{I_{MD} \eta_{MD} e_{WS}}{N_A z} = \frac{(V - 2.3 + \eta_A - \eta_C) \eta_{MD} e_{WS}}{\left[\frac{\pi D_P^2 \varepsilon^3 (P_O - P_L)}{144 \Lambda (1-\varepsilon)^2 \tau \mu} \left(\frac{l_s}{l_D} + 1 \right) + R_m \right] N_A z} \quad (15)$$

Thus in the limit as every other sources of inefficiency (side reactions, physical loss of products outside the cell, measurement errors, effect of the separating medium) tends to zero, the modelled current efficiency obtained from the modelled volumetric flow rate, current and the GDOCE can also be expressed as:

$$\eta_{MD} = \frac{\dot{m}_{MS}}{\dot{m}_{HS}} \quad (16)$$

The observed operational current efficiency could be obtained from the theoretical production rate expected from the observed operational current (I_{OB}), and the observed production rate of caustic soda($\dot{m}_{OS}$). The theoretical production rate expected from the observed operational current is given as:

$$\dot{m}_{TH} = \frac{I_{OB} e_{WS}}{F} \quad (17)$$

Therefore the observed operational current efficiency is given as:

$$\eta_{OB} = \frac{\dot{m}_{OS}}{\dot{m}_{TH}} = \frac{C_{OS} \dot{V}_{OB} F}{I_{OB} e_{WS}} \quad (18)$$

The observed production rate of caustic soda is given as:

$$\dot{m}_{OS} = C_{OS} \dot{V}_{OB} \quad (19)$$

Therefore the observed operational current efficiency is given as:

$$\eta_{OB} = \frac{\dot{m}_{OS}}{\dot{m}_{TH}} = \frac{C_{OS} \dot{V}_{OB} F}{I_{OB} e_{WS}} \quad (20)$$

$$\text{Molarity} = \frac{C_{OS}}{40} \quad (21)$$

$$\text{Experimental specific electrical energy} = \frac{P_{OB}}{\dot{m}_{OS}} \quad (22)$$

$$\text{Modelled specific electrical energy} = \frac{P_{MD}}{\dot{m}_{MS}} \quad (23)$$

$$\text{Yield} = \frac{\dot{m}_{OS}}{\text{inlet mass flow rate of brine feed}} \quad (24)$$

$$\text{Yield /d.c Watt} = \frac{Yield}{P_{MD}} \quad (25)$$

The deviation (ΔE_X) of modelled value ($\bar{X}_{MD}$) from corresponding experimental value (X_{EXP}) is given as:

$$\Delta E_x = \frac{X_{MD} - X_{EXP}}{X_{EXP}} \quad (26)$$

IV. Results and Discussion

It was observed for all operations that the open circuit voltage was always greater than the cell voltage at loading. This was because of the fact that loading caused a drop in potential, in addition to the effect of the charge controller on the cells also. The charge controller was needed to regulate the amount of current entering into the cell, and also to prevent the backward flow of electricity from the cell to the solar panels as a result of the electrochemical potential generated in the cell by reason of the electrochemical reactions. Furthermore, it was observed that the amount of electricity generated by the solar panels varied with the intensity of the sun on each particular day. The highest voltage was observed for the hottest day and vice-versa. The values of current, mass flow rate, efficiency and so on obtained for the

three cells closely resemble the range obtained for diaphragm cells operated by stepped down a.c to d.c rectified power supply from mains and solar powered cells (Olufemi et al, 1999, 2000, 2008, 2011). The applicable simulated values were estimated at their corresponding experimental counterparts as presented from Equations 1 to 26. The simulated values were estimated algebraically from the appropriate relationships and validated with their corresponding experimental values. The variation of average current with average voltage for all the non-asbestos diaphragm cells is shown in Figure 3. Higher currents with corresponding voltages were observed for the diaphragm cells as the weight percent of the cement reduces, while those of silica and PVC increases. The cells confirmed the ohmic direct proportional relationship that current increases linearly with voltage. The non-asbestos cell with diaphragm D1 seems to have a higher operational electrical resistance with respect to the present operation. The simulated values matched the experimental values closely.

In Figure 4, the molar concentration of caustic soda in the catholyte products of the three cells is shown to increase with average cell current. The cell with non-asbestos diaphragm D1 produced more concentrated solutions relatively than the others with respect to the present electrochemical operation. Despite the fact that the cell with Diaphragm D1 operated at a higher electrical current than its counterparts at corresponding voltages, it still produced more concentrated products. The cell with diaphragm D1 seems to be better in the production of more concentrated product in this regard. The reason may be due to the fact that the diaphragm is less permeable than the others resulting in relatively higher residence time of the reacting species at the electrodes. This means that conversion will be higher per unit space volume of cell. The modeled values seem to closely match the experimental counterparts for all the diaphragm cells.

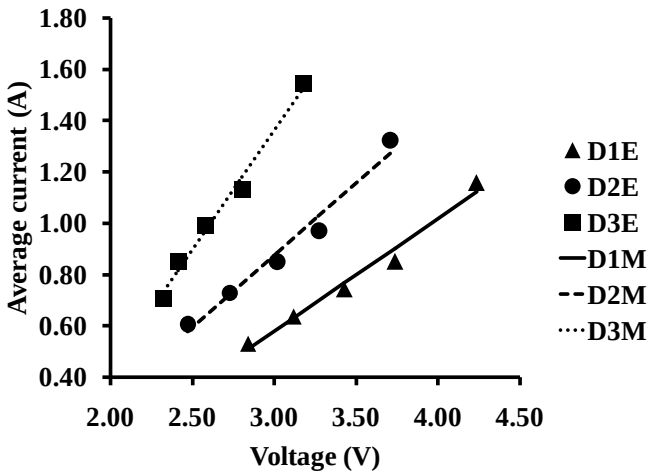

Figure 3 : Variation of current with voltage for the non-asbestos diaphragm cells

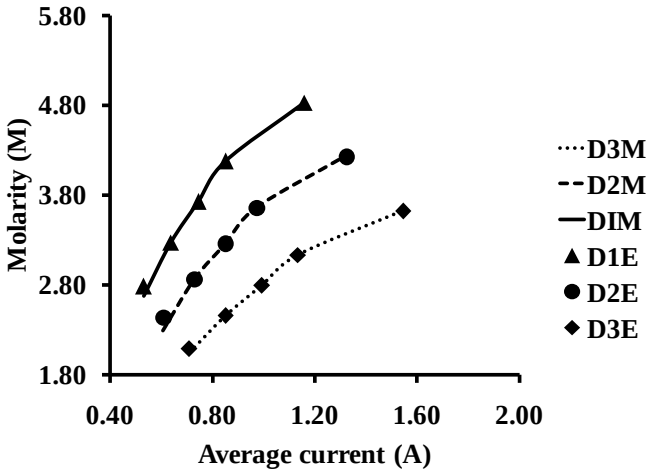

Figure 4 : Variation of concentration with current for the non-asbestos diaphragm cells

Variation of the mass flow rate of caustic soda produced for the two cells with average operational current is plotted in Figure 5. As expected from the previous plot, diaphragm D3 electrochemical cell resulted in higher mass flow rate than the other cells. This follows directly from the fact that this diaphragm is more permeable in the present operation. However it can be observed in the three cells that the mass flow rate increased to a maximum value and then declined. This means that operation at too high current values can lead to energy wastage if not controlled. This is a subject of optimum cell design and optimum cell operation. The simulated values matched the experimental values perfectly with the deviation less than ± 6 %.

The variation of average current efficiency with operational voltage is shown in Figure 6. As it can be deducted from the operation of the cells, too high voltage above the theoretical decomposition voltage leads to reduction in efficiency, thereby resulting in more energy wastage. The diaphragm D3 cell recorded the highest current efficiencies with respect to the present operational procedure. The relatively higher permeable nature and relatively lower operating voltage of the diaphragm may be responsible for its higher current efficiency relative to other counterparts. As depicted also, the simulation closely predicts the experimental values.

The yield (kg NaOH / kg NaCl input) increased with voltage in Figure 7, with that of the non-asbestos diaphragm D3 cell indicating higher yield with respect to operational voltages recorded. This showed the possibility of improving the yield of caustic soda produced with increased operational voltages for the cells. The simulated values seem to match the experimental values perfectly.

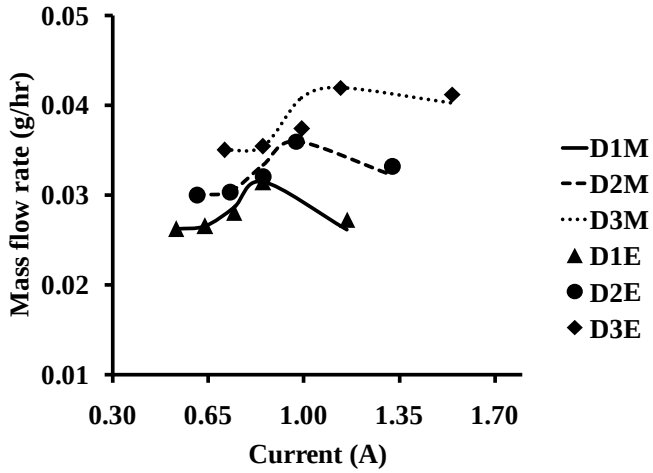

Figure 5 : Variation of mass flow rate with current for the non-asbestos diaphragm cells

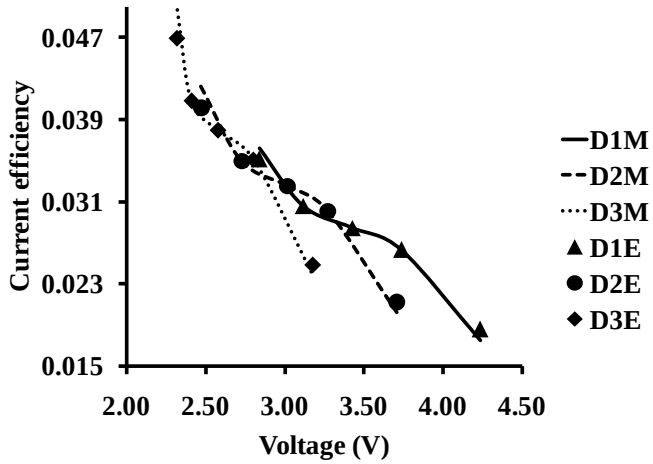

Figure 6 : Variation of current efficiency with operational voltage for the non-asbestos diaphragm cells

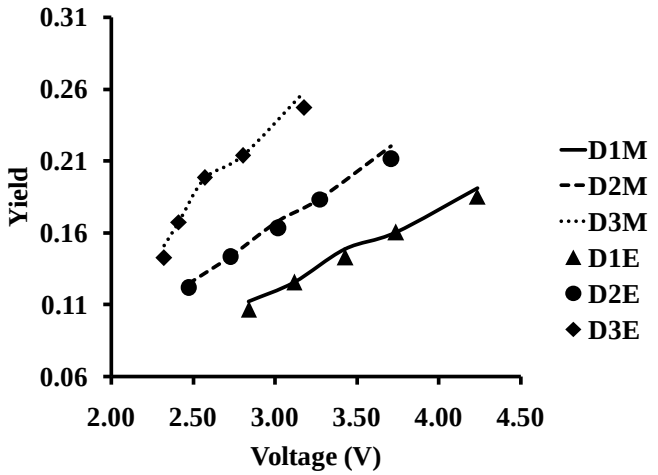

Figure 7 : Variation of yield with operational voltage for the non-asbestos diaphragm cells

In Figure 8, the non-asbestos diaphragm D3 cell showed a better yield per d.c Watt than the other cells. This indicated that the cell in the present operation produced more desired product than the other cells at corresponding electrical d.c power supplied. The yield / d.c Watt is a good indication of the electrical power effectiveness of substance producing electrochemical cells. The maximum positive and negative deviations of simulated from experimental data was between +0.06 and -0.05 respectively.

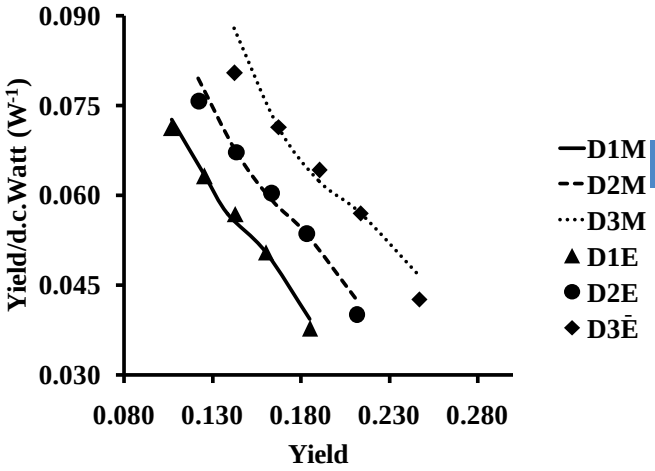

Figure 8 : Variation of yield with yield/d.c Watt for the asbestos and non-asbestos diaphragm cells

In Figure 9, the variation of the yield with specific electrical energy for the production of caustic soda is shown. It can be deduced that the yield increases with the specific electrical energy needed to produce 1 kg of caustic soda the three cells. From the plot, the yield seems higher with the specific energy required by the non-asbestos diaphragm D3 cell in comparison with other cells. This is a strong indication that if improved upon, these non-asbestos diaphragm cells have a higher capability of producing more caustic soda for the same electrical energy supplied. In comparison with industrial cells, the specific energy required by commercial diaphragm cells approximately varies from 1.38 x 10^7 to 2.03 x 10^7 J / kg, with current densities ranging between 900 to 2600 A / m^2 (Worell et al, 2000; Tilak et al, 2007). The three laboratory scale cells presented here required higher specific energy per kilogram of caustic soda produced in the present operation. The current densities employed in the solar powered cells ranged from 55.21 to 160.42 A / m^2, which is relatively lower to commercial diaphragm cells current densities. This is likely to be the reason for the relatively higher specific energy required per kilogram of caustic soda produced. Appropriate scale-up and optimization techniques of the solar powered cells could make the values comparable. The simulation seems to closely predict the experimental values.

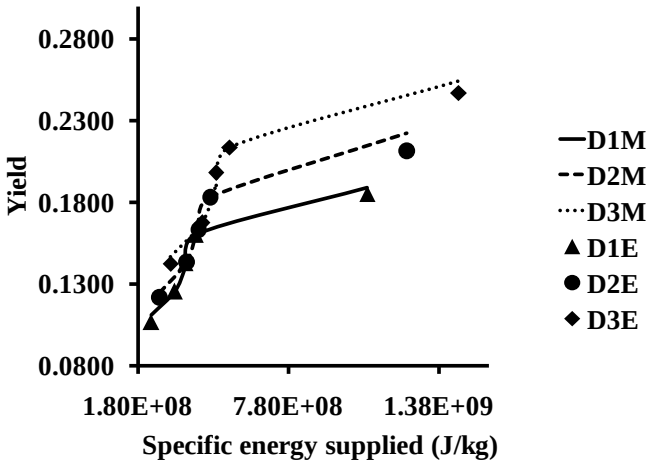

Figure 9 : Variation of yield with specific electrical energy for the non-asbestos diaphragm cells

V. Conclusion

From the results obtained, the modeling and simulation presented in this work closely predicted the cell operations, as the maximum positive and negative deviations of simulated from experimental data was between +0.07 and -0.06 respectively. From the results obtained from the cell operations, it can be reasonably concluded that the non-asbestos diaphragm D3 cell seems to be more preferred, because its yield and productivity is comparatively better to that of other non-asbestos diaphragm cells. This reflects its higher permeability due to the lower percentage of Portland cement and higher percentages of PVC and silica relative to others.

As observed, a solar powered diaphragm cell is capable of producing caustic soda of specification closely equal to those produced by conventionally powered diaphragm cells of similar scale, as long as the solar panels are capable of generating enough voltage to overcome cell and circuit resistance by situating it in an appropriate location, installing them correctly, and completing the circuit as required. The advantages of the present work are that the cells can be operated without the use of conventional electric power, since the only energy required comes directly from the sun. Also the operation can be a very compact process that fits into a small area or can be scaled up to the required size depending on the capacity of production. The process promised to be very economical and very flexible in terms of expansion. The operation is environmentally friendly, because the only form of energy required is solar. The disadvantages of the operation are that it is not highly efficient after sunset and during rainfall. Also, production is not constant but depends on the sun's intensity.

With further research on appropriate scale-up and optimization techniques, solar powered cells could possibly match commercial scale conventional cells in certain performances. The maximum current density employed was 160.42 A / m^2 for the three cells combined together. This is low compared with those employed in conventional commercial diaphragm cells which in many cases range from 900 to 2600 A / m^2 (Worell et al, 2000; Tilak et al, 2007). However, a very important factor which the solar powered cells are expected to achieve is to have a high output of material for little input of material and energy, which is the recent trend in the chlor-alkali industry, according to Minteer (2002) and Sugiyama et *al.* (2003).

Above all, this direct solar energy powered means of producing caustic soda with electrochemical cells could be a very commercially viable project in areas where the power situation is epileptic, erratic and undergoing reforms, considering the fact that those areas might need to have abundant sunlight for better part of the year.

Acknowledgement

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Symbols

A_A, A_{AC}, A_C, A_D, A_{EL}, A_{IA}, A_{IC} = Area (m^2)
C_{OS} = Observed caustic soda concentration (kg/m^3)
D_P = Pore Diameter (m)
e_{WS}, e_{WE} = Equivalent weight (kg/kgmol)
F = Faraday's Constant (C/mol)
g = Acceleration due to gravity (m/s^2)
h_t = Height of anolyte (m)
I_{MD}, I_{OB}, I_{MN} = Current (A)
l_D = Diaphragm thickness (m)
l_S = Distance between electrodes (m)
k = Average electrolyte specific conductivity ($Ohm^{-1}m^{-1}$)
m = Ionic mobility of hydroxyl ion (m/s)(V/m)
$\dot{m}_{OS}$, $\dot{m}_{OB}$, $\dot{m}_{HS}$, $\dot{m}_{MS}$ = Mass flow rate (kg/s)
N_A = Avogadro's number
P_O, P_L = Pressure (N/m^2)
P_{MD} = Modelled Power (Watt)
R_m = Resistance (Ohm)
r_{RA}, r_{RC} = Reaction rate (mol/m^2s)
T = Temperature (K)
t = time (s)
v, V = Volume (m^3), Voltage (V)
$\dot{V}_D$, $\dot{V}_{OB}$ = Volumetric flow rate (m^3/s)
w = Percentage weight
z = Electron Charge (C)

Greek Alphabet

ρ_{EL} = Density of electrolyte(kg/m^3)
τ = Tortuosity factor
ε = Porosity
Λ = Equivalent Conductance (Ohm^{-1} m^2)
η = Overvoltage (V)
η_{MD}, η_{OB} = Current efficiency

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A Survey of Generator Maintenance Scheduling Techniques

By Dr. Al-Arfaj Khalid & Karamitsos Ioannis
Rayadah Investment Company (RIC), Riyadh, Saudi Arabia

Abstract - Many maintenance-scheduling methods have been proposed using conventional mathematical programming methods or heuristic techniques. Heuristic approaches provide the most primitive solution based on trial-and-error approaches. Mathematical optimization based techniques are completely distinct from classical programming and trial-and-error heuristic methods. These techniques have been proposed to solve small maintenance scheduling problems. In this paper we explain the difference between both methods in solving generator maintenance scheduling (GMS) problem.

Keywords : *Maintenance, Scheduling, Mathematical Heuristics Techniques.*

GJRE-J Classification: *FOR Code: 091399*

Strictly as per the compliance and regulations of:

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Dr. Al-Arfaj Khalid [α] & Karamitsos Ioannis [σ]

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I. Introduction

Heurestic techniques may not generally lead to the global optimal for a complex problem, i.e. the procedure tends to fall into a local minimum if a starting point is not carefully chosen. Heuristic methods were used earlier in solving maintenance scheduling problems for centralized power systems because of their simplicity and flexibility. Mathematical optimization based techniques such as integer programming [24], dynamic programming [61-60] and branch-and-bound [43] have been proposed to solve maintenance scheduling problems. For small problems these methods give an exact optimal solution. However, as the size of the problem increases, the size of the solution space increases greatly and hence the running time of these algorithms. These approaches tend to suffer from an excessive computational time with the increase of variables. To overcome this difficulty, modern techniques such as simulated annealing [13-37], stochastic evolution [52], genetic algorithms [32] and Tabu search [51] have been proposed as alternatives where the problem size precludes traditional techniques. These techniques are completely distinct from classical programming and trial-and-error heuristic methods. The GA methods mimics the principles of natural genetics and natural selection to constitute search and optimization procedures. Simulated annealing mimics the cooling phenomenon of molten metals to constitute a search procedure.

The GA and SA approaches have been reported to solve a range of optimization problems in electrical power systems with encouraging results (Mirinda et al.. [43]). The following sections review the some of common math-base and modern heuristic based techniques. The paper is organized as follows: In Section II we presented mathematical techniques, in section III an artificial intelligence approach is described and the conclusion in section IV.

II. Mathematical Techniques

The Mathematical approaches are mainly based on linear, Integer, and Mixed-Integer Programming (LP, IP, and MIP), Decomposition, Branch-And-Bound (BaB) and Dynamic Programming (DP). In the following sections we describe several mathematical solution techniques, which were used in the literature for solving maintenance scheduling problems.

In the following figure the mathematical techniques are presented.

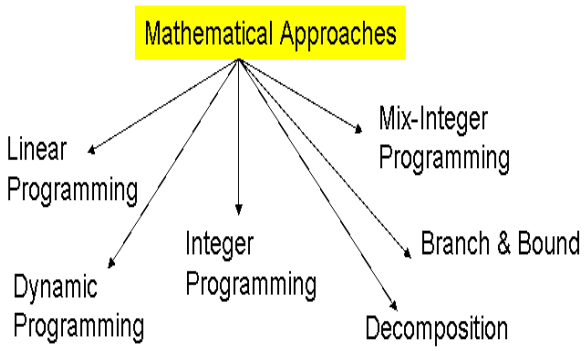

Figure 1 : Mathematical Approaches

a) Linear, Integer, and Mixed-Integer Programming

The most basic mathematical programming technique is linear program (LP). It has been applied with impressive success to problems ranging from familiar cases in industry, economics and transportation to the more extreme cases in behavioral sciences [45]. The LP model refers to an optimization problem in which the objective function and the constraint function are linear variables. Integer programming (IP) is essentially LP with the additional requirement that the variables have to be an integer. If only some of the variables are required to be integer and the others are real, then it became mixed integer programming (MIP). Combinatorial scheduling problems can often be formulated as IP or MIP problems [34],[7],[24].

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The cutting plane (polyhedral) technique deals with IP by focusing on LP relaxation. The techniques aim at generating additional linear constraints that have to be satisfied for the variables to be integer. These additional inequalities constraint the feasible set more than the original set of linear inequalities without cutting off integer solutions. Solving the LP relaxation of the IP with additional inequalities then yields a different solution, which may be integer. If the solution is integer, the procedure stops, because the solution obtained is an optimal solution for the original IP. If the variables are not integer, more inequalities are generated [50]. In any LP there is a dual problem to the primary one. These two problems are related to each other with interesting applications. The duality in LP has been used in another solution technique, Benders decomposition.

Shahidehpour and Marwali [54] in their book have used MIP and the Benders decomposition technique to coordinate and optimize maintenance scheduling in a deregulated system.

Yao et al.[46] have developed a model based on mixed integer programming and it is helpful in resource limitations in manufacturing. The non linear functions appearing in the MIP model can be transformed into linear functions with the help of decision variables. This can be solved by using any LP/IP software. The result shows that in the PM based model scheduling system, the equipment availability would increase and become profitable to the manufacturer.

b) Dynamic Programming

In 1957, Dynamic Programming (DP) originates from Bellman and is applicable to a lot of optimizing problems, not just those arising in scheduling [28]. It is one of the more widely used techniques for solving combinatorial optimization problems. DP can be applied to problems that are solved in polynomial time as well as problems that can't be solved in polynomial time. It has proven to be applicable to stochastic problems as well [50].

Dynamic programming is basically a complete enumeration scheme that attempts, with a divide-and-conquer approach, to minimize the amount of computation to be done. The approach solves a series of sub problems until it finds the solution of the original problem. It determines the optimal solution for each sub problem and its contribution to the objective function. At each iteration, it determines the optimal solution for a sub problem, which is better than the previously solved sub problems. It finds a solution for the current sub problems by utilizing all the information obtained before in the solutions of all previous sub problems as well [50].

c) Branch and Bound

The Apart from heuristic methods, the Branch-and-Bound (BaB) technique is probably the most widely used technique in scheduling. Like DP it is an enumeration technique and used to optimize large class problems [28]. It is a type of implicit enumeration method or tree search method, which can find an optimal solution by systematically examining subsets of feasible solutions [43-14].

The Branch-and-Bound procedure consists of the repeated application of the following steps. First, that portion of the solution space (i.e. set of decision variables under consideration) in which the optimal solution is known to lie is partitioned into subsets. Second, if all of the elements in a subset violate the constraints of the minimization problem, then that subset is eliminated from further consideration (fathomed). Third, an upper bound on the minimum value of the objective function is computed. Finally, lower bounds are computed on the value of the objective function when the decision variables are constrained to lie in each subset still under consideration. A subset is then fathomed if its lower bound exceeds the upper bound of the minimization problem, since the optimal decision variable cannot lie in that subset. Convergence takes place when only one subset of decision variables remains and the upper and lower bounds are equal for that subset [49].

d) Benders Decomposition

Bender's method, based on LP duality theory, decomposes the scheduling optimization problem into a master problem and several sub-problems. The master problem in this case involves only the integer variables of the problem, and the sub-problems involve only the continuous variables. The solution process of the master problem starts with almost no constraints. Then the sub-problem is used as a test to check if this solution satisfies the remaining constraints. If so, then the solution is optimal, since the objective has been minimized over all constraints. Otherwise, the most unsatisfied constraint (i.e. the deepest cut) will be added to the master problem, and it will be resolved with the added constraint. The main disadvantages of this approach are the long computational time requirement and the suitable problem model [54].

Because of the combinational nature of the GMS problem, MIP and Bender's decomposition methods are used to coordinate and optimize maintenance schedules. Marwali and Shahidehpour [40] use Benders decomposition for solving maintenance scheduling problems for centralized power system structures. They use Benders decomposition to decompose a complex Integrated Maintenance Scheduler (IMS) problem that represents a network constrained generation and transmission maintenance-scheduling problem, into a master problem and operation sub-problems. By using an IMS, several and complex constraints which bound the selection of scheduling times, are included into the solution method. In this problem, at each iteration, the solution of sub-

problems generate dual multipliers, which are used to form one or more constraints that will be added to the master problem for the next iteration until a feasible solution is found. Benders approach has been used in different publications [54-42] for solving different problems in deregulated systems. Also, Marwali and Shahidehpour, [41] have used Benders decomposition method to solve a short-term transmission maintenance problem.

III. Artificial Intelligence Approach

Various Artificial Intelligence (AI) techniques for solving the maintenance-scheduling problems of a power system can be found in the literature with different presentations. Artificial Intelligence (AI) includes expert systems, Simulated Annealing (SA), fuzzy logic theory, neural network, evolutionary optimization including evolutionary programming, evolutionary strategy and Generic Algorithm (GA), simulated evolution and their hybrids. This section will present some of theses AI techniques.

a) Simulated Annealing (SA)

Kirkpatrick et al.,[37] and Cerny, [13] independently introduced simulated annealing. Satoh and Nara, [53] and Burk et al.,[9] have considered simulated Annealing (SA) algorithms in solving thermal generator maintenance scheduling problems. The problems were formulated using the economic objective and typical problem constraints. The authors found that SA was faster than integer programming (IP) in finding the same solution for their small and medium-sized problems. Also, the SA approach was able to find a solution for the large system where IP could not be realized due to combinatorial explosion. They used a binary string representation to encode a trial solution and penalty approach to take account of the problem constraints [20].

Annealing, physically, refers to the process of heating up a solid to a high temperature followed by slow cooling achieved by decreasing the temperature of the environment in steps Wong and Wong [57] and Annakkage et al. [4]. By making similarity between the annealing method and the optimization problem, an enormous class of combinatorial optimization problems can be solved following the same procedure of conversion from one equilibrium condition to another, reaching minimum energy of the system [49]. The initialization of the SA method involves the selection of an initial temperature (T_0) and an initial solution in the search. The initial solution may be generated at random or by any other means. If the final solution is to be independent of the starting solution, the initial temperature (T_0) must be high enough to permit an almost free switch of neighbouring solutions. Generally the value of (T_0)is chosen in such a way that it is greater than the maximum possible difference between the evaluation values of two solutions [25].

Finally, the criterion for stopping the algorithm can be articulated either in terms of a minimum value of the temperature, or in terms of the 'freezing' of the system at the current solution. 'Freezing' may be recognized by the number of iterations (or 'temperatures') that have passed without a move being acknowledged that has exceeded a given limit, or by the number of accepted moves in a stage falling below a given value. However, the simplest rule of all is to fix the total number of iterations. The number of iterations needs to be carefully tuned with other parameters to make sure that it corresponds to a satisfactorily low temperature to ensure convergence [21].

Then, the temperature is decreased as the algorithm progresses according to a cooling schedule. The cooling schedule may be adapted by using a large number of iterations at a small number of temperatures or vice versa. The number of iterations at each temperature and the rate at which the temperature is reduced are significant factors in controlling the performance of the SA method. The number of iterations increases with successive temperatures since it is important to spend more time searching at lower temperatures to guarantee that the neighborhood of a local optimum has been entirely explored. Then, the move operator specifies the algorithm for generating a new trial solution from the current solution. Randomly, the move operator selects one variable from the integer strings to be changed. The selected variable is then changed to a random value in the allowed range.

b) Genetic Algorithms (GA)

During the last years, there has been a growing interest in problem-solving systems based on the principles of evolution and machine learning [48-55]; where such systems maintain a population of potential solutions. They have some selection process based on fitness of individuals and some "genetic" operators [49]. In the 1970s, Holland [44] introduced the concept of a genetic algorithm (GA). Like other Artificial Intelligence (AI) the basic idea behind GA was to make computers do what humans do. In order to apply a genetic algorithm to solve an optimization problem, candidate solutions must be encoded using an appropriate representation, such as a numeric string, and an evaluation function must be formulated to assign a quality value to every solution produced.

The GA represents an iterative process, where each iteration is called a generation. Population size specifies how many individuals there are in each generation. With a large population size, the genetic algorithm searches the solution space more thoroughly, thereby reducing the possibility that the algorithm will return a local minimum that is not a global minimum. However, a large population size also causes the algorithm to run more slowly. Each population contains a number of chromosomes, and a chromosome consists of several "genes", and each gene is represented by 0 or 1.

There are two basic mechanisms that link a GA to the problem it is solving: encoding and evaluation. The encoding is carried out using binary strings (chromosomes) of ones and zeros in each bit, which is the most popular representation. An evaluation function is used to measure the chromosome's performance, or fitness, on the problem to be solved. The GA uses a measure of fitness of individual chromosomes to carry out reproduction. Genetic algorithms apply three genetic operators: selection, crossover and mutation.

i. *Selection Genetic Operator*

There are different types of selection methods [5] such as the following:

- Tournament selection: where a small subset of individuals is chosen at random, then choosing the best individual from that set to be a parent.
- The roulette wheel selection: The most common chromosome selection technique is the roulette wheel selection [32-22]. Roulette selection chooses parents by simulating a roulette wheel, in which the area of the section of the wheel corresponding to an individual is proportional to the individual's expectation. For example, for a given population each chromosome is given a slice of a circular roulette wheel equal to the chromosome fitness ratio. To select a chromosome for mating, a random number is generated, and the chromosome whose segment spans the random number is selected. It is like rotating a roulette wheel where each chromosome has a section on the wheel proportional to its fitness. The roulette wheel is spun, and when the arrow comes to stop on one of the slices, the corresponding chromosome is chosen.

ii. *Cross over*

Crossover specifies how the genetic algorithm combines two individuals, or parents, to form a crossover child for the next generation. The crossover operator is applied with a certain crossover probability, once a pair of parent chromosomes is selected. Generally, a value of 0.7 for the crossover probability produces good results [46]. First, the crossover operator randomly chooses a crossover point where two parent chromosomes "break", and then exchanges the chromosome parts after that point. As a result, two new off-spring are created. There are different types of crossovers for example [5]:

- Single point crossover: where a single locus chosen at random then a parent chromosome break and all bits after that point be swapped.
- Two point crossover: this involves choosing two points at random and swapping the corresponding parts from the two parents defined by the two points.

iii. *Mutation*

Mutation specifies how the genetic algorithm makes small random changes in the individuals in the population to create mutation children. Mutation can occur at any gene in the chromosome with some probability. Typically, the mutation probability is in the range between 0.001 and 0.01.

Mutation provides genetic diversity and enables the genetic algorithm to search a broader space [47]. Genetic algorithms guarantee the continuous improvement of the average fitness of the population, and after a certain number of generations the population evolves to an optimal or near-optimal solution.

Given a clearly defined problem and a binary string representation for candidate solutions, a basic GA can be represented in the following steps [22-44]:

Step 1: Represent the problem variable domain as a chromosome of and define the population size, the crossover and the mutation probability, and the evaluation function.

Step 2: Randomly produce an initial population of chromosomes.

Step 3: Compute the fitness of each one.

Step 4: Choose a couple of chromosomes for mating.

Step 5: Generate a pair of offspring chromosomes by applying genetic operators.

Step 6: Position the formed offspring chromosomes in the new population, then repeat Step 4, until the size of the new population becomes equivalent to the size of the initial population.

Step 7: Substitute the initial (parent) chromosome population with the new (offspring) population.

Step 8: Go to Step 3, and repeat the process until the termination criterion is fulfilled.

Genetic algorithms become popular as a powerful optimization tool appropriate for a diversity of problems. Both GA by it self or a combination of GA and other techniques are broadly addressed in the literature for solving maintenance scheduling for power systems. Negnevitsky and Kelareva [47] have used GA is solving maintenance scheduling in power systems. The objective was to maximize reserve margins subject to maintenance and system constraints. They have designed a representation which is suitable for a variety of problems and appropriate chromosome evaluation is suggested. A case study was solved using GA, and the result shows that chromosome representation plays an important role in GA where it may reduce problem complexity by including constraints. Abdulwhab et al.[1] use the genetic algorithm optimization technique to maximize the overall system reliability for a specified future time period in which a number of generating units are to be removed from service for preventive maintenance.

Baskar et al.[6] has used GA with modified genetic operators, such as string reversal and reciprocal exchange mutation, to solve the generator maintenance scheduling (GMS) problem. They have used three types of encoding; integer encoding, binary for integer

encoding, and real encoding. The GMS problem is solved to minimize the expected energy production cost and maximizing the reserve objectives subject to maintenance windows, consecutive periods of maintenance, crew, demand reserve and reliability. The result shows that only integer coding GA finds the global optimum solution, irrespective of the nature of the objective function and system size. Also, modified genetic operators were shown to be effective in reducing computation time and improving search efficiency of the GA.

It has been reported that the performance of the GA approach can be improved by combining it with other techniques [51]. The GA/SA hybrid approach has been employed to solve a maintenance scheduling problem by Kim et al., [36]. The hybrid approach presented by Mohanta et al. [45] use the integer encoding for solving the captive power plant maintenance scheduling problem with levelized reserve reliability objective function. From the comparison of results obtained from application of only GA and from hybrid GA/SA techniques for scheduling, can be seen that the hybrid GA/SA solution technique yields better results.

Dahal et al.[20] investigated the applications of GA and SA using an integer representation to encode candidate solutions to GMS test problems with a reliability criterion. The evaluation function is a weighted sum of the objective function and the penalty function for violations of the constraint. The authors concluded that the SA and GA are robust and stable techniques for solving GMS problems.

Dahal et al. [17] propose solving centralized maintenance problems using GA with integer's representation using fuzzy evaluation functions. Since fuzzy logic can be used to deal with multiple objectives, it was used to combine the objective of maximizing reliability and considering the flexibility in the manpower constraint. The fuzzy evaluation function is developed as a combination of a crisp penalty function for inflexible load constraint and a fuzzy penalty function for the objective and the flexible manpower constraints. The results obtained using the fuzzy logic evaluation function were compared with those obtained from GAs with crisp evaluation functions, and the fuzzy logic method was shown to achieve an effective trade-off between reliability and manpower within the allowed flexibility.

Burk and Smith [12] presented a technique named Memetic approach for solving real scale maintenance scheduling problems in centralized structures. The objective was to minimize the sum of the overall fuel and maintenance costs. Memetic is a genetic algorithm combined with Tabu search. Tabu search is a powerful optimization procedure that has been successfully applied to a number of combinatorial optimization problems. Memetic takes the concept of evolution as employed in GA. It has a memory as unit of information instead of gene in GA [23]. A population of information can be created and a good one has a better chance of survival than a bad one, and they can be combined to form new ideas. They investigated the use of Memetic algorithms for solving thermal generator maintenance scheduling problems. A comparison between Tabu search and Memetic algorithm shows that Tabu is more affective for small problems and Memetic algorithm will outperform Tabu search for large problems. Also, they show that the Memetic algorithm using Tabu search as the local optimizer yields greater benefits than simulated annealing which was used previously in solving thermal generator maintenance scheduling problems [53].

c) Multi-stage Approach

A new solution approach was developed by Burk and Smith [11] for solving large size thermal generator maintenance scheduling problems for centralized structures. It is named multi-stage approach. The problem which has been solved by the authors has been tackled by different researchers using different solution techniques such as SA, GA, Memetic and Tabu. Among these algorithms the Memetic algorithm alone can produce quality solutions at the expense of extended run-time. The authors addressed the problem of extended run-times by using a multi-stage approach. Instead of solving the problem in one step, the multi-stage approach segregates the main problem into a series of sub-problems, each can be solved consecutively then the results recombined to form the solution of the original problem. It is not suitable for indivisible problems. It is similar to the rolling-horizon technique, which has been applied to problems such as multipurpose plant scheduling ,commercial fishing fleet scheduling and production scheduling.

The first task of the multi-stage algorithm is to order the units according to some measure of difficulty. An example of the difficulty measure is ordering the units with the least number of possible maintenance starting periods first. Another example is scheduling the units with the highest operating capacity first. In doing so the chance of creating difficulties later on in the process is decreased. Then, the algorithm will fit the easier units in the available gaps. The multi-staging approach picks the first N units and schedules them using the Tabu search or Mimetic algorithm. All other units are left unscheduled. The next N units (most difficult units to schedule) are then placed in the schedule, and so on, until all units have been scheduled. Therefore, each evaluation function can re-use data acquired from the previous evaluation very effectively.

This approach differs from other rolling horizon approaches in that the problem is divided into sub-problems which contain a reduced number of units to be scheduled, rather than sub-problems with a look-ahead set of a further M units from the list to the units currently being scheduled. However at the end of the scheduling, only the first N units are fixed into the schedule. This enables the algorithm to schedule the current set of N units based not only on the units already

scheduled (if any), but also to utilize additional information based from looking ahead at the next M units [11].

IV. Conclusion

There are many solution methods, in this paper we reviewed a wide range of mathematical and artificial intelligence approaches. In the literature, these techniques were used to solve different maintenance scheduling problems.

Heuristic methods were used previously in solving maintenance scheduling problems because of their elasticity, but they may not lead to optimal solution for a complex problem. Mathematical techniques such as MIP and Bender's Decomposition, have been proposed to solve generator maintenance scheduling problems for small problems. However, for NP-complete scheduling problems traditional deterministic techniques can fail due to time limits.

Genetic Algorithm (GA) becomes a powerful optimization tool appropriate for a diversity of problems. Gas are based on natural genetic and evolution mechanisms which can be used to solve complicated optimization problems. The key success of GA lies in defining a fitness function that incorporates all constraints. Genetic Algorithm (GA) was found to be a powerful optimization tool for solving different maintenance scheduling for power systems.

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Adsorption of Heavy Metals from Waste Waters on Tea Waste

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Abstract - Heavy metals in particular are a group of pollutants of major concern in the aquatic environment due to their toxicity. The need to find an inexpensive and effective method for heavy metals abatement from water becomes inevitable. Adsorption in very effectively used technique for this purpose but cost is an important parameter and the types of adsorbents conventionally used are expensive. The aim of this study is to use the tea waste as a low cost adsorbent for the removal of metal concentration in industry effluents. The effect of variation in different parameters like initial concentration of metals in solution, adsorbent amount and contact time were investigated. The adsorbent is very effective for lower concentration of metal solutions, and the adsorbance increases with increase in adsorbent dose. Around 96% removal of lead, 78% removal of nickel and 63% removal of cadmium is obtained using 0.5 gm of adsorbent and the efficiency is increased to 100% for Pb, 87% for Ni and 83% for Cd, by using 1.5 gm of the adsorbent. As this adsorbent is cheap and easily available, it can be used in little excess amount to obtain higher percentage of metal removal. A comparative study for removal efficiency for Pb, Ni, Cd is also discussed. The adsorbent prepared from tea waste is efficient and it is proposed that it can be conveniently employed as a low cost alternative in the treatment of waste water for heavy metal removal.

Keywords : *adsorption, heavy metals, tea waste adsorbent, waste water.*

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I. Introduction

Industrial waste constitutes the major source of various kinds of metal pollutants in natural water [1]. This water pollution due to toxic heavy metals has been a major cause of concern for scientists. It is adversely affecting the health of the people and also damaging the environment [2]. Metals can be distinguished from other toxic pollutants, since they are non biodegradable and can accumulate in the living tissues. The important toxic metals Cd, Ni, Pb etc. find their way to the water bodies through waste waters [3]. The release of large quantities of these metals into the natural environment, for eg. irrigation using sewage water, results in environmental contamination [4], and the metals due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain and pose a danger to human health [5] [6]. Generally heavy metals are present in low concentrations in waste waters and are difficult to remove from water.

Many physico-chemical methods have been proposed for their removal from industrial effluents [7]. Commonly used methods for separation and removal of metals are extraction, precipitation, crystallization, ultra-filtration, carbon adsorption etc. [8]. But these conventional methods are neither much effective nor economical. Adsorption is an effective technique used in industry especially, in water and waste water treatment [9]. Cost is an important factor for comparing the sorbent materials [10]. The commercially used carbon adsorbents are expensive. Now-a-days various low cost adsorbents are investigated. The agricultural water products are much widely being studied for their adsorption efficiency. These products are readily available and low in cost also. Researchers have been done on many such materials like sugarcane, bagasse, straw, wool fiber, leaves, jute coir, rice husk, saw dust, cotton seed hulls etc. [11], [12]. Coal and straw are inexpensive but ineffective. Peat moss has been found effective in adsorbing heavy metals [13], coconut shell [14], saw dust [15], and crop milling waste [16], [17] also gave good results.

In recent years tea waste is also gaining grounds as an efficient adsorbent for removal of metal ions from waste waters due to its potential to overcome these pollutants. Insoluble cell walls of tea leaves are largely made up of cellulose, lignin, tannins and structural proteins imparting it good potential as metal scavenger from solutions and waste waters since the above mentioned constituents contain the functional groups, mainly carboxylate, phenolic hydroxyl and oxyl groups. Very few investigations have used tea waste as an adsorbent for removing heavy metals [18]. Mahavi et al. used tea waste as an adsorbent for the removal of heavy metals from industrial waste. Malkoe and Nuhoglu investigated the removal of nickel from aqueous solutions using tea factory waste.

In this work, the efficiency of tea waste as an adsorbent has been determined in the process of removing heavy metals from aqueous solutions. The effect of various parameters such as initial concentration of metals in solution, adsorbent dose and the contact time has been studied.

II. Materilas and Methods

For the adsorption experiments carried out tea waste has been used as adsorbent. Tea waste used was washed several times with distilled water. It was

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then dried in an oven at 120°C and then ground and sieved on a screen with mesh size 40.Individual solutions of Ni, Pb, Cd with 4 different concentrations were prepared (5, 10, 20, 30 mg/l) synthetically. The experiments were conducted to determine the efficiency of tea waste in adsorption of metals from their aqueous solutions. The effect of initial concentration of metals, the effect of adsorbent dose and the contact time were observed by conducting different sets of experiments.

The experiments were performed in three parts. Firstly 12 flasks were taken, each containing 0.5 gm adsorbent. 100 ml of solutions with known concentratios of lead were added (5, 10, 20, 30 mg/l) to four sets of three flasks each. Thereupon we had 3 similar concentrations for each experiment, for eg 3 flasks containing 5 mg/l, 3 containing 10 ml/l, 3 containing 20 ml/l and the remaining 3 having 30 mg/l lead.

All these flasks were located on a shaker with 150 rpm. Four flasks with different solution concentration were removed after 15 minutes. The contents were filtered through Whitman no. 40 filter paper to prevent the probable interference of turbidity. The lead concentration of the filtered solutions was then determined using atomic adsorption spectrophoto - meter. The same procedure was repeated after 30 min. and then after 1 hour from the starting. The readings for lead concentrations in terms of the percentage removal are reported.

These experiments were repeated for an initial adsorbent dose equal to 1gm and also for 1.5 g. The data for lead removal by adsorption are given in table 1.The same complete procedure was then done with Ni and also with Cd solutions. The percentage removal of these metals by adsorption on tea waste adsorbent is reported in table 2 for Ni and in table 3 for Cd.

III. Results and Discussion

As the results of this study show, the adsorption efficiency is found to be maximum for Pb and minimum for Cd(evident from Table 1, 2 and 3).

Table 1: Percent removal of lead by adsorption

Adsorbent dose 0.5 gm				
Time (min)	Initial concentration of lead (mg/l)			
	5	10	20	30
15	51.3	42.5	40.7	35.6
30	86.2	83.2	78.4	72.3
60	96.2	90.5	85.1	83.2
Adsorbent dose 1 gm				
Time (min)	Initial concentration of lead (mg/l)			
	5	10	20	30
15	56.2	53.1	51.1	49.1
30	90.7	88.8	85.3	75.2
60	99.1	98.9	97.6	88.7
Adsorbent dose 1.5 gm				
Time (min)	Initial concentration of lead (mg/l)			
	5	10	20	30
15	60.5	52.2	49.1	45.3
30	93.8	90.3	89.2	79.1
60	100	100	99.4	97.6

Table 2 : Percent removal of Nickel by adsorption

Adsorbent dose 0.5 gm				
Time (min)	Initial concentration of Ni (mg/l)			
	5	10	20	30
15	43.8	40.2	37.4	30.5
30	61.3	58.5	50.5	48.3
60	78.2	71.5	68.1	59.2
Adsorbent mass 1 gm				
Time (min)	Initial concentration of Ni (mg/l)			
	5	10	20	30
15	49.8	46.3	40.1	33.7
30	68.5	61.4	55.2	50.8
60	89.6	80.3	75.1	71.2
Adsorbent dose 1.5 gm				
Time (min)	I Initial concentration of Ni (mg/l)			
	5	10	20	30
15	55.7	49.2	45.1	39.4
30	74.9	68.3	61.7	54.9
60	87.1	85.6	80.2	79.1

Table 3 : Percent removal of cadmium by adsorption

Adsorbent dose 0.5 gm				
Time (min)	Initial concentration of Cd (mg/l)			
	5	10	20	30
15	35.6	30.2	25.9	19.1
30	54.5	45.3	35.7	27.3
60	63.5	53.9	45.4	35.3
Adsorbent dose 1 gm				
Time (min)	Initial concentration of Cd (mg/l)			
	5	10	20	30
15	41.6	37.2	28.9	23.5
30	66.4	54.7	38.8	37.6
60	76.2	63.1	51.3	48.2
Adsorbent dose 1.5 gm				
Time (min)	Initial concentration of Cd (mg/l)			
	5	10	20	30
15	49.5	40.2	35.4	29.3
30	73.7	66.1	56.7	48.2
60	83.4	75.6	65.5	60.1

The rate of adsorption depends on the adsorbent amount and the initial concentration of metal in solutions and also on time of contact.

Tables 1-3 show the percent removal of metals. The data table of amount of metal adsorbed at various intervals of time, indicates that the removal of metal initially increases with time but the rate of adsorption decreases with time. It is evident from the data that the % removal of lead is 51.3 in first 15 minutes and reaches 96.2% in 60 minutes. The adsorption process was found to be very rapid initially and a very large fraction of total concentration of metal was removed in the first 30 minutes. The initial concentration of metal in solution affects greatly on the asorption rate. Though it was observed that the rate of adsorption of metals increased with an increase in initial concentration in the solution which shows the dependency upon the concentration of metal solution, but overall the percentage removal of metal decreases with the increase in metal concentration. For a particular experiment the rate of adsorption decreases with time. It gradually approaches a maximum adsorption; owing to continuous decrease in the concentration driving force and it also indicate that the adsorbent gradually becomes saturated. The adsorbent shows a great capacity for adsorption of metals for lower solution concentrations. The data also reveals the effect of various mass of adsorbent on the percentage removal of the metals. The tables also show a decreasing trend in metal concentration at a faster rate as the adsorbent mass is increased. Initially the rate of increase in the percentage metal removal has been found to be very fast but slowed down with the increase in the adsorbent dose.

This can be explained that at lower adsorbent mass, the metals are readily accessible and the removal of metals per unit mass of adsorbent is greater. The overall increase in adsorption by increasing the adsorbent amount seems to be an effect of increase in adsorption sites. Thereby it is possible to have increased adsorption by further reducing the particle size of the adsorbent. As we see 96.2% removal of Pb was possible from a 5 mg/l solution with 0.5 gm adsorbent but for 30 mg/l solution, 0.5 g adsorbent just gave 83.2% removal, but by increasing the amount of adsorbent to 1.5 gm it was possible to increase the efficiency of adsorption upto about 97.6% for the same 30 mg/l solution. Similar trends are observed for Ni and Cd. Larger surface area of adsorbent favours adsorption so the rise in adsorption with an increase in adsorbent dose is due to bigger driving force and larger surface area. Mahavi et al [18] used tea waste as an adsorbent for the removal of heavy metals (Cd, Pb, Ni) from industrial waste water. Their results showed 94-100% removal of lead, 86% removal for Ni and 77% for Cd, using tea waste as adsorbent and the present work in comparison gave better efficiency. The reason for this increase in percentage removal of metals may be explained firstly by the smaller particle size of the adsorbent that give rise to larger surface area available for adsorption of heavy metals and secondly by the higher speed of rotation on shaker, which causes more contact of metal ions with the adsorption surface. So we would have better treatment by using excess amount of tea waste adsorbent or by reducing the particle size of adsorbent and also using higher rpm on shaker. As this adsorbent in cheap and easily available, therefore there is no problem in increasing its consumption for better results. By comparing the data in all three tables. It is also found that adsorption efficiency is dependent on the type of metal too. As we can note that the percent removal for Pb are maximum than for Ni and it has been noted the minimum for Cd.

For Pb, an initial concentration of 5 mg/l with 1.0 gm adsorbent shows a removal of 98.2%. For Ni in similar conditions it reaches upto just 87.3% and for Cd, it shows upto 73.2% removal in same time and similar conditions of initial concentration and amount of adsorbent.

IV. Conclusion

Analysis of the results of this study indicates that tea waste can be used in the treatment process of heavy metals like the many other low cost natural adsorbents. Though, the initial concentration of metals in waste water solution, greatly affect the efficiency of its removal. This can give very high efficiency by precise choosing of the adsorbent quantity. Tea waste is a low cost material and easily available. So it can be very conveniently used for treating the industrial waste water as an efficient adsorbent for the heavy metals

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Lean Sigma- Not just a whim. It is here to Stay

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Abstract - The aim of this paper is to illustrate the evolution and brief history of Lean and Six Sigma and trace it to its role at present. Also, the paper gives its arguments why they are not mere whims or fads that fade away with the passage of time. The findings in the paper suggest that the implementation of these philosophies of management in industries and other business processes help these enterprises in the reduction of cost and in the of working on improvement of the quality issues. Thus using these two strategies, either individually or together to maximize the gain of an organization may be a logical conclusion. In the present work, we have tried to show that these two strategies are helpful to satisfy cost and quality constraints whether related to products or services and are not just fads, as have been considered to be by some of its critics.

Keywords : *Lean manufacturing, Six sigma, Value-stream mapping, DMAIC.*

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Lean Sigma- Not just a whim. It is here to Stay

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I. Introduction

Improvement is needed today, perhaps more than ever before. Various methodologies have been used over the years to improve businesses. Each new approach has its building blocks on the previous approaches but also goes a step ahead from its predecessor by adding new concepts, apart from adopting the effective aspects and eliminating the limitations of the older approach. Dean (1997) showed in his work that Taylor had begun the improvement as we know about it today, with his work on scientific management. Later during the century, during the difficult financial times cash flow became essential to keep an organization running. The lean six sigma approach is the latest among the approaches of process improvement. The greatest advantage of this approach is that it improves bottom-line results that are needed to fuel innovation and growth and as well as enhancing customer satisfaction. Apart from this Lean Six Sigma has also been widely accepted as an effective leadership tool. Lean Six Sigma works better than previous approaches because it integrates the human and process aspects of process improvement.

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II. Lean -A Historical Perspective

The roots of lean management originated from the Toyota production system (TPS), a manufacturing philosophy conceptualized by the Japanese engineers Taiichi Ohno and Shigeo Shingo (Inman, 1999) and the concept of mass production was established in the early 19th century by Henry Ford (1913). The development of this approach of manufacturing began soon after the Second World War when companies were faced by acute shortage of capital as well as resources. Eiji Toyoda, employed by the Toyota Motor Company, instructed his workers to eliminate all waste. Furthering on this philosophy, through a process of trial and error a new manufacturing system, also known as Toyota Production System was achieved. This lean operations management design approach, which was adapted by US as the Just in Time Approach (JIT), focused on the elimination of waste and excess from the tactical product flows at Toyota and represented an alternative to mass production. Holweg (2007) showed that Lean manufacturing extends the scope of the Toyota production philosophy by providing an enterprise-wide term that draws together the five elements of "the product development process, the supplier management process, the customer management process, and the policy focusing process for the whole enterprise" .The main target of lean, as defined by Hines and Rich (1997) is value stream (identifying value-added and non-value added activities), and to eliminate all waste, or muda, in all areas and functions within the system. Seven forms of waste have been identified as;

1) Over-production;
2) Defects;
3) Unnecessary inventory;
4) Inappropriate processing;
5) Excessive transportation;
6) Waiting; and
7) Unnecessary motion.

Womack and Jones(1990) identify five key principles of the lean organization

1) The elimination of waste (or muda);
2) The identification of the value stream;
3) The achievement of flow through the process;
4) Pacing by a pull (or kanban) signal; and
5) The continuous pursuit of perfection.

Rother and Shook (1999) showed the emergence of Value stream mapping for the role to identify value added and non-value adding processes. VSM brings together all of the lean techniques like the provision of a common language when considering manufacturing processes. In the initial period of awareness of lean during the 1990's, the main weaknesses of lean manufacturing were its automotive manufacturing-based view and limited appreciation of how to handle variability in demand. The implementation was tool-focused, and generally neglected the human aspects of the high-performance work. Later on, after the 1990's; there was a widening of focus away from the shop floor. After 1990, there was a gradual widening of focus away from the shop-floor. This evolution focused on quality during the literature of the early 1990s, through quality, cost and delivery in the late 1990s, to customer Value from 2000 onwards. Hines et.al (2004) has identified the concept of Lean to have undergone a significant evolution and expansion beyond its origins in the auto industry, and its narrow definition around shop-floor improvement.

a) Shortcomings of Lean

1. Implementation of Lean is costly and time consuming.
2. There is still a fair deal of misunderstanding of the contingent nature required to apply Lean thinking.
3. Lean is often criticized to be de-humanizing and exploitative because of the high pressure it puts on the shop floor workers to achieve the highest output.

III. Six sigma- A Historical Perspective

Barney (2002) quoted Six Sigma as strategic, company-wide, approach. It focuses on variation reduction that gives projects the potential of simultaneously reducing cost and increasing customer satisfaction. The approach originated in Motorola in 1987. Six Sigma was conceptualized as a quality goal in the mid- 1980s at Motorola because technology was becoming so complex that traditional ideas about acceptable quality levels were inadequate. As the number of opportunities for defects increased, the percentage of perfection had to rise. In 1989 Motorola announced a five-year goal—a defect rate of not more than 3.4 parts per million—six sigma. This initiative challenged ideas of quality in the U.S. and changed the concept of quality levels. It was quickly no longer sufficient to measure quality as percentages (defects per hundred opportunities). Now the bar was raised, to measure defects per million or billion. In 1994 Larry Bossidy, CEO of Signal, introduced Six Sigma as a business initiative to ''produce high-level results, improve work processes, expand all employees' skills and change the culture''. Later on, the implementation of Six Sigma at General Electric began in 1995. Schroeder et al. (2008) have identified various elements of Six Sigma programs such as management involvement, improvement specialists, performance metrics, a systematic procedure, and project selection and prioritization. Rajagopalan et. al. (2004) argued Six Sigma programs improve operational performance in order to enhance customer satisfaction with a company's products and services. Six Sigma has today evolved into a business improvement system that has taken hold at many high-performing organizations. Thomas and Fisher (2007) mentioned six sigma organizations use the five-step DMAIC (pronounced "da-MAY-ik") as shown in fig.1. The root of Six Sigma lies in the concept of total quality management where everyone in an organization is responsible for the quality of goods and services produced by the organization. Sower et. al. (1999) concluded other components of Six Sigma that can be traced to Total Quality Management (TQM) include the focus on customer satisfaction when making management decisions, and a significant investment in education and training in statistics, root cause analysis, and other problem solving methodologies.

Fig. 1 : The DMAIC model

Revere et. al. (2002) concluded Six Sigma has evolved over the years, which now includes designing, improving, and monitoring business processes. Now it becomes multifaceted, encompassing everything from simple process improvement to broad initiatives, such as project management, change management, leadership, culture change, rewards and compensation, defect definition, teaming, and problem solving. Applications of six Sigma span over a variety of industries, from the manufacturing sectors like Motorola and GE mentioned in Pande et. al (2000) construction industry mentioned in Stewart and Spencer (2006) and accounting practices mentioned in Brewer and Bagranoff (2004) as well as in the service sector mentioned in Chakrabarty and Tan (2007).

a) Shortcomings of Six Sigma

1. Antony (2004) focuses the adverse effect of colour qualification belts in six sigma (green, black, master black belts etc.) used for training effects as non standardized and can be source lead to bureaucracy within an organization and thus drive the focus away from the performance issues.
2. The organizational improvement philosophy of Six Sigma is still not well understood or explored and thus faces the threat of being oversold or incorrectly used.
3. Use of Six Sigma for solutions and as well as its training can be expensive for many businesses.
4. Six Sigma alone cannot dramatically improve process speed or reduce invested capital.

IV. Lean Six Sigma: What And Why

Sheridan (2000) described the "lean Six Sigma" phrase as the integration of lean and Six Sigma philosophies. Lean Six Sigma is a business strategy and methodology that increases process performance resulting in enhanced customer satisfaction and improved bottom line results. With disparate roots but similar goals, Six Sigma and lean management are both effective on their own. However, some organizations that have adapted either Six Sigma or lean management might eventually reach a point of diminishing returns. In order to improve business processes on some periodic basis, all organizations need a methodology for problem solving and improvement. A systematic approach to improvement is needed to improve performance as measured by quality, cost, delivery and customer satisfaction. Bottom line improvements also provide the cash needed to fuel innovation and growth. Bendell (2006) has stated that the concept of lean Six Sigma as an approach to process improvement has yet to fully mature into a specific area of academic research. Smith (2003) said that in practice the majority of efforts to fully and comprehensively implement a lean Six Sigma initiative to its full potential have not been realized. Cusumano, (1994) regarded as a failure to sustain a change towards continuous improvement can be attributed for one, to the lack of commitment from management. Bendell, (2006) quoted that in the case of fusing lean and Six Sigma, the two approaches have often been implemented in isolation, creating lean and Six Sigma subcultures to emerge within the organization, which can conflict of interest and a drain on resources. The integration of lean and Six Sigma aims to target every type of opportunity for improvement within an organization. Smith (2003) stated Six Sigma is only implemented by a few specific individuals within a company, lean levels the empowerment and education of everyone in the organization to identify and eliminate non-value adding activities. The integration of the two methodologies attempts to provide empowerment even at the higher-level process analysis stages, so that employees have true ownership of the process. Figure 2 summarizes the nature of improvements that may occur in organizations that practice lean management or Six Sigma, and the corresponding improvements that an integrated program could offer. The horizontal axis represents the customer's perspective of value, including quality and delivery performance. The vertical axis represents the producer's cost to provide the product or service to the customer. Under either system, improvements will be made, but a improvements will begin to level off at a certain point in time. With Six Sigma alone, the levelling off of improvements may be due to the emphasis on optimizing measurable quality and delivery metrics, but ignoring changes in the basic operating systems to remove wasteful activities. Higgins (2005) argued that with lean management alone, the leveling off of improvements may be due to the emphasis on streamlining product flow, but doing so in a less than scientific manner relating to the use of data and statistical quality control methods.

A Lean Six Sigma (LSS) organization would capitalize on the strengths of both Lean management and Six Sigma. A LSS Organization would include the following three primary tenets of lean management:

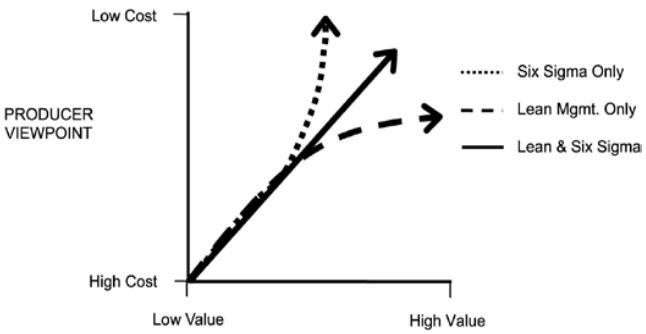

Fig. 2 : Customer View Point Source Arnheiter and Maleyeff (2005)

1) It would incorporate an over-riding philosophy that seeks to maximize the value-added content of all operations
2) It would constantly evaluate all incentive systems in place to ensure that they result in global optimization instead of local optimization.
3) It would incorporate a management decision-making process that bases every decision on its relative impact on the customer.

Similarly, a LSS organization would include the following three primary tenets of Six Sigma:

1) It would stress data-driven methodologies in all decision making, so that changes are based on scientific rather than ad hoc studies.
2) It would promote methodologies that strive to minimize variation of quality characteristics.
3) It would design and implement a company-wide and highly structured education and training regimen.

V. Lean Six Sigma - Not Just a Whim

Gibson and Tesone (2001) stated that it is often argued that a method that is marketed and promoted as new is actually a reassembled version of a previous method. The early disintegrating fads leave their remnants that under new names become new fads. Abrahamson (1996) stated that these fashion-like cycles may be created by organizations continually searching for improvement in their operations. New procedures may be adopted when they are widely hailed as solutions to human and organizational problems, and then dropped after the promised results fail to materialize or are superceded by another. However, improvement approaches come and go, but improving the bottom line never goes out of style. The integration of Lean Six Sigma is not just about Lean Six Sigma, but addresses a major issue which is the improvement of business processes. The financial crisis is encouraging leaders and organizations to view Lean Six Sigma as an approach to reduce costs and keep the cash flowing. Lean Six Sigma is the method to realize improvement. The supporters of Lean Six Sigma have given numerous arguments as to why this is not just a fad. To further justify this argument, a look at what fads are is important. Fads tend to follow a seven-stage life cycle:

1) An academic article is written on a new discovery or theory;
2) The study is discussed, summarized, and repeated;
3) The concept is popularized in a best-selling book;
4) Throngs of management consultants carry the new technique to their client base;
5) Managers embrace the fad and champion the concept;
6) Time passes, enthusiasm dims, and doubts and cynicism arise; and
7) New discoveries occur and consultant interest turns elsewhere.

However, over the years both Six Sigma and lean management have evolved into comprehensive management systems. These philosophies have not suddenly emerged, but over the years, through trial and errors have undergone several changes to now encompass common features, such as an emphasis on customer satisfaction, high quality, comprehensive employee training and empowerment. These goals are not time or demand specific, but are the basic building blocks that are highly critical to the success of an organization. It can be argued that these goals are essential to the growth and success of an organization and any management strategy that offers solution at this grass root level is likely to survive beyond the hype that is associated with a fad. An increase in productivity is the ultimate solution that the combination of lean six sigma offers.

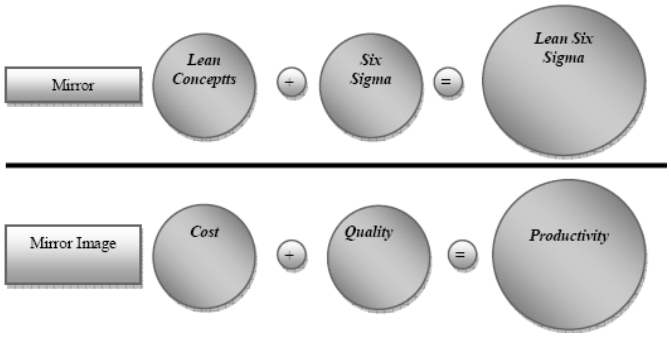

Fig.3 : Productivity a Reflection of Lean Six Sigma

As shown in figure 3 while cost can be considered as mirror image of Lean, and quality that of Six Sigma, the combination of the two, i.e., cost and quality helps in increasing productivity. Although to maximize the advantages from Lean Six Sigma method, it is important to implement the two policies harmoniously, so that it can achieve both strategic and operational improvement in productivity.

VI. Bridging the Gap Between Lean and Six Sigma

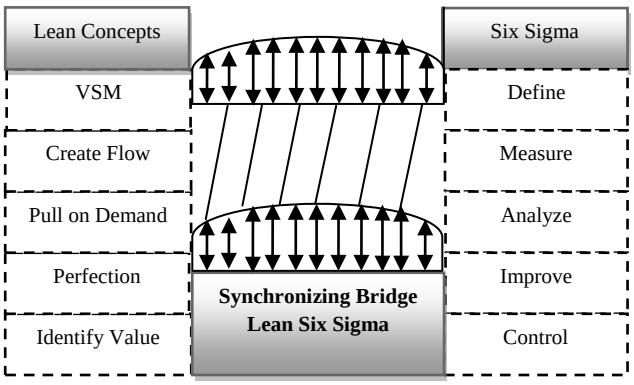

Fig.4 : Lean Six Sigma Bridge

Figure 4 reflects the five main tenets of both Lean and Six Sigma. The main features of Lean are to help in reducing cost, whereas the key principles of Six Sigma are used to reduce the variability of products. However, in any organization or industry the main aim is to ultimately improve the quality of its products or services. These issues can be addressed only by reduction in costs achieved by application of Lean and as well as process improvement by reducing variability to the six sigma levels.

VII. Methods and Methodology

The author shortlisted 25 major industries in and around Delhi, India that were using Lean and/or Six Sigma as their company policy. The questionnaire that was used for the purpose of the study was tested for

reliability using Cronbach's alpha test. The questions were designed such that they all had a standardized Cronbach's alphas range from a low of 0.74 to a high of 0.84. The questionnaire formulated was then sent to the selected industries through mail. Out of the industries selected, only 10 responses were received. The main purpose of the questionnaire was to know about the experiences of these industries in using Lean and/or Six Sigma, either together or as separate entities. The first part of the questionnaire asked the individual respondent about the position they occupied in the company. It was observed that the employees belonged to different levels of the industrial hierarchy from shop floor technicians to the production managers. The next part of the questionnaire addressed questions about how the companies became aware of either lean or Six Sigma and also the duration from which they were using it. The respondent companies were then asked about their reasons and experiences of the implementation of either lean and/or six sigma in their companies and also on the reasons for further using these in the future considering the advantages it gave in the cost reduction and quality issues. The individual questions were designed such that the respondents had to give their responses to the questions or statements on a 5 point Likert scale (1-5) starting from 'Very high to Very low' as two extremes of continua, that were divided in five intervals of measurement. In addition, the approximations were used in terms of numbers and/or percentages for measurement.

VIII. Results

Based on the results of the questionnaire it was seen that considering the fact that lean six sigma is a relatively new policy, it has already been adapted by a significant number of major industries in northern India. It was also seen that most of the industries became aware of this policy through professional papers and other such publications. By the responses given, it was observed that the respondent companies were using this policy for more than a year and the most common reasons for using the policy were to improve customer satisfaction and remain competitive in the international market. The companies were seen to have a positive experience of using lean six sigma and were convinced of using it in the future because of the advantages it gave them in maintaining their quality and eliminating waste and thus helping in cost reduction. On the basis of all the results that were obtained with the help of the questionnaire the following conclusion was made.

IX. Conclusion

Over the years several management approaches and solutions have been offered in order to increase the outputs of an organization and to gain maximum customer satisfaction. Several of these have been unable to retain with the due passage of time. However, as can be concluded from the results of the present study, unlike such previous concepts, Lean Six Sigma can be considered to be fairly successful in helping organizations achieve their targets. From the responses given it can be seen that the industries had used lean six sigma before and were convinced of using it in the future as well. Companies and organizations are always in lookout for methods to improve their productivity which Lean Six Sigma can definitely provide them with. At the end of the paper, it can be concluded that a policy like lean six sigma that has its fair share of supporters who have been using it and hope to continue doing so in the future, is definitely not a fad as it has been considered by some of its critics and it holds the key for managing the cost and quality issues of industries, and specially so for those in the developing countries.

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Modification of the Chemico-Physical Properties of Sewage Sludge towards its Application for Agricultural Purposes

By Rosik-Dulewska Cz, Nocoń K & Karwaczyńska U
University of Opole, OleskaSt

Abstract - Municipal sewage sludge belongs to organic waste rich in organic matter, nitrogen and phosphorus and at the same time poor in potassium content. From the environmental viewpoint, sewage sludge should be recovered as fertilizer i.e. utilised for land applications. However, in order to do so, the sludge cannot contain heavy metals in amounts above the permitted levels.The article presents the results of a research carried out to investigate the potential of utilizing sewage sludge of high fertilizing values and elevated zinc content for agricultural purposes by mixing it in appropriate ratio with fly ash from lignite and hard coal combustion and granulation. Data from tests on enriching the sludge-fly ash mixtures with potassium to improve its fertilizing properties are also presented. The research was carried out taking into account relevant regulations effective in the EU countries. The investigations proved that sewage sludge can be successfully mixed with fly ash in weight proportion 1:1 and granulated while maintaining the minimum content of organic matter, nitrogen and phosphorus required for organic-mineral fertilizers and meeting the level of heavy metals permissible for sludge used for agricultural purposes. However, due to low potassium content in sludge-fly ash mixtures, an addition of potassium salt is proposed at maintaining simultaneously the proportion of sludge to ash as 7:3. The procedure for utilizing sewage sludge, a problem-causing organic waste, described in the paper shows that it is possible to produce an organic-mineral product of desired chemical properties for soil conditioning which through the granulation process acquires also a physical form and mechanical properties making it easy to transport and apply.

Keywords : *sewage sludge, fly ash, modification, agriculture.*

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Keywords : sewage sludge, fly ash, modification, agriculture.

I. Introduction

Management of the sewage sludge produced in increasing volumes from year to year due to sanitation of urban and rural settlements poses a serious challenge. The problem is not only the volume of the sludge itself but its quality as well. Due to the soil-forming and fertilizing values of sewage sludge resulting from high content of nitrogen, phosphorus, magnesium, calcium and microelements, its land application seems one of the most efficient solutions [13]. At the same time however, an increasing awareness of risks posed by introducing sewage sludge into the soil environment evokes serious concerns among scientists and farmers. For several years there has been a tendency in Europe to strengthen the regulations allowing for sewage sludge application to the soil environment to better protect it. The EU proposed an amendment of the Directive 86/278/EEC of 12 June 1986 on the protection of the environment and the soils when using sewage sludge (biosolids) as a fertilizer [2]. In 2000 a third draft of the working document concerning this amendment was issued (ENV.E.3/LM) [15]. The changes proposed in the sludge directive refer mainly to more stringent requirements concerning heavy metals content (Table 1) and introduction of a monitoring of organic pollutants. The document indicates the need to extend the scope of the effective legal regulations and performance of sewage sludge management in such areas as forests, green areas and areas for reclamation. It states that sewage sludge should find application whenever an increase of yields or soil fertilization are needed. When applying sludge, other legal acts should be also taken account of, especially Directive 91/676/EEC concerning water protection against pollution caused by nitrates originating from agricultural sources. Manner in which the sewage sludge is utilized should ensure a minimal negative effect on human and animal health, plants, quality of ground and surface water; soil quality in a long-time perspective and biodiversity [1]. Due to planned restrictions concerning permissible heavy metals content in sewage sludge introduced to the soil, more restrictions should be expected in the stabilized sludge application for agricultural purposes, especially in the case of sludge originating from municipal and industrial wastewater treatment plants that contains high amounts of heavy metals which are not categorised as plant nutrients (mercury, lead, cadmium). Sewage sludge containing excessive amounts of these heavy metals which are indispensable for plants can be used for production of microfertilising preparations and enrichment of basic fertilisers in microelements (e.g. zinc, copper, manganese, iron). Reduction of heavy metals concentration can be achieved by adding a foreign matter to the sludge e.g. an addition of plant mass

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followed by composting of both components. Also liming is an example of heavy metals concentration reduction in sludge [14]. Another practice consists in mixing sewage sludge with fly ash, especially from lignite, which is rich in calcium compounds. However, its should be underlined that mixing sewage sludge with lime or fly ash reduces the content of organic matter and the fertilising components in a dry unit of the product. Nevertheless, sludge mixing with fly ash has a number of benefits. The binding properties of ash allow for a good solidification with sludge. The alcalescent properties of ash and its fine-grain form enable eliminating the risks posed by pathogens contained in sludge and reduce odour emission. Also a sanitation effect of the fly ash admixture to the sludge is known which reduces the washout of chemical contaminants while improving the physical and mechanical properties of the sludge [3,4,10,11,12]. The use of a special process line with drum, plate or matrix granulator allows achieving an appropriate form, size and mechanical stability of the sludge-ash mixtures which make their transport and application easier [3,8]. The goal of the research presented in this paper was to modify the physico-chemical properties of a stabilised sewage sludge with zinc content exceeding the permissible level for agricultural sludge application in such a way as to achieve a product which could be used in agriculture.

II. Materials and Methods

The following materials and components were used in the tests: (i) stabilised sewage sludge originating from the Zabrze-Śródmieście wastewater treatment plant (ii) fly ash from lignite combustion originating from the Bełchatów power plant and fly ash from hard coal combustion originating from the Ł aziska power plant (iii) hydrated lime (iiii) potassium chloride of potassium content of 60% recalculated to k_2o. the modification of the physico-chemical properties of the sewage sludge was carried out in the following way:

1. Fly ash was added to a pre-dried sewage sludge of a 50% dry matter content. Next the mixture was homogenised and granulated in a plate granulator with a regulated rotation speed and plate angle of 1m. The produced granulate was dried to the dry mater content level of ca 98%. Three granulates were prepared: N9 with lignite fly ash and sewage sludge content in weight proportion as 7:3, N10 with lignite fly ash and sewage sludge content in weight proportion as 1:1, and N14 with hard coal fly ash and sewage sludge content in weight proportion as 3:7.

2. Sewage sludge pre-dried to dry matter content of ca 50% was mixed with fly ash and hydrated lime, then granulated in a granulator with ring matrix of 8mm aperture diameter. The obtained granulate was dried to the dry matter content of ca. 95%. Two granulates were prepared: N41 with lignite fly ash and N42 with hard coal fly ash. The weight ratio of ash to sludge in both granulates was as 7:3, while the amount of the added hydrated lime was 3,3% by weight of the ash dry mass.

3. Sewage sludge pre-dried to the dry mass content of ca. 50% was mixed with potassium chloride, then with fly ash and hydrated lime. Next, the procedure was similar as in point 2. Two granulates were prepared: N41/m with lignite ash content and N42/m with hard coal ash content. The weight ratio of sludge to ash in both granulates was as 7:3, while the amount of hydrated lime was 3,3% by weight of the ash dry mass and the potassium chloride was 300 g/km of dry mass of the other components.

The contents of organic matter, nitrogen, phosphorus, potassium and heavy metals were determined in the investigated sewage sludge, fly ash and in the granulates. The chemical composition of the fly ash was determined applying the procedure of an accredited Laboratory of Carbochemistry IChPW Q/ZK/P/15/01/B „Determination of the chemical composition of ash by roentgen fluorescence" using Philips energy dispersive MiniPal spectrometer and the norm PN-G-04528-10:1998 "Solid fuels. Determination of the chemical composition of ash. Determination of disodium oxide (Na_2O) and dipotassium oxide (K_2O)" using flame photometry on BIOTECH Management AFP spectrometer. The content of organic matter in sludge and granulates was determined according to the norm PN-75/C-04616.01 "Water and wastewater. Special sludge tests. Determination of water, dry mass, organic substance and mineral substance in sewage sludge".

The content of Kjeldahl total nitrogen in the sludge and granulates was determined according to the norm PN-75/C-04576.17 "Water and wastewater. Investigation of nitrogen compounds content. Determination of Kjeldahl total nitrogen in sewage sludge". The content of phosphates in the sludge and granulates was determined according to the norm PN-75/C-04537/14 "Water and wastewater. Investigation of phosphorus compounds content. Determination of total phosphates in sewage sludge by titration". Potassium content in the granulates modified with potassium salt was determined according to the norm PN-75/C-04591.05 "Water and wastewater. Investigation of potassium ion content. Determination of potassium ion content in sewage sludge by weight method". To determine the total content of metals: copper, zinc, nickel, lead, cadmium, chromium and potassium in the sludge and granulates, atomic absorption spectroscopy (AAS) was applied using UNICAM –PHILIPS PU9100 X spectrometer. Following the reference method as specified in the Regulation on municipal sewage sludge, prior to the determination the samples were extracted in aqua regia. [6]. Mercury content was determined in air dry samples according to the methodology recommended by the Polish Geological Institute using AMA 254 mercury analyser.

III. Research, Results and Discussion

The sludge used for the tests originated from a mechanical-biological wastewater treatment plant located in an industrial part of an urban agglomeration. Considering its land application, in particular for agricultural purposes, some limitations may appear, mainly due to a significant content of one or more heavy metals in the sludge mass. Typically however, the composition of sewage sludge undergoes seasonal changes resulting from the quality of the influent. The properties of the sewage sludge applied in the described research are presented in Table 2 and 3. The sewage sludge was rich in organic matter, its content amounted to 58% d.m. The content of nitrogen and phosphorus in the sludge was on the medium level of these biogenes content determined in sludge from municipal wastewater treatment plants in Poland [5], and amounted 3,6% d.m and 2,9 % d.m., respectively. Typically for municipal sewage sludge, the content of potassium was low i.e. 0,21 % d.m. Among metals contained in the sludge zinc was dominant. Following the Regulation [6], its content on the level of 3567 mg/kg d.m. allows for sludge application for specific needs resulting from the waste management plans, spatial development plans or decisions concerning building conditions and land management, for plants cultivation for composting purposes as well as purposes other than consumption or fodder production. At the same time the content of other heavy metals in the sludge was low, which would enable its agricultural application. To extend the scope of its potential land applications, the sludge was mixed with fly ash from coal combustion. Fly ash admixture to the sludge enables reduction of heavy metals concentration through the so called heavy metals dilution process, so that they are no longer a barrier in sludge application for agricultural purposes. Two types of fly ash were used in the investigations, their selected properties are presented in Table 2 and 3. Coal combustion processes taking place in the furnace cause that trace amounts of organic matter and nitrogen occur in fly ash. The content of phosphorus in fly ash from hard coal was higher compared to its content in the fly ash from lignite, whereas potassium content in the fly ash from lignite was comparable to its content in the sludge and nearly ten times higher in the fly ash from hard coal. Except for copper, the content of the determined metals was higher in the fly ash from hard coal combustion compared to the corresponding values in the fly ash from lignite. Comparing the content of heavy metals in the fly ash and in the sludge, higher values for nickel and chromium were determined in the sludge, however metals from the fly ash were extracted with a stronger extractant (see the section on methodology). It should be thus expected, that the tested mixtures of sewage sludge and fly ash will be characterised by lower fertilising values and higher nickel and chromium content than the sludge alone. These differences will increase with a raising content of fly ash in the mixtures. Simultaneously however, higher amounts of fly ash added to the sludge allow achieving a beneficial effect of the reduced zinc content i.e. the metal dominant in the sludge. However, due to the adopted assumption that the final product (sludge-ash granulate) should meet the effective legal regulations for land application, the content of the fertilising components should be in line with the requirements specified by the Regulation of the Ministry and Rural Development on the execution of selected provisions of the Act on Fertilising and Fertilisers [7] as well as the requirements of the Regulation of the Minister of Environment on the municipal sewage sludge [6]. An additional issue discussed by the authors in another publication [9] was to obtain a product of appropriate physical qualities (granulation and mechanical durability) to enable its storage, transport and application. Tables 4 and 5 present the data from the tests as described in the section „Materials and methods" on the fertilising qualities and standardised heavy metals content of the granulated sludge-ash mixes. Sludge is the component that impacts the fertilising quality of the granulate. Therefore these mixtures that contained the highest amount of sludge i.e. N14, N41 and A 42 (sludge to ash weight ratio as 7:3) showed the highest contribution of the organic matter (41,2-43,5%), total nitrogen (2,32-2,41%) and phosphorus in oxide form (5,18-6,09%). The fertilising qualities of the other granulates were lower, nevertheless still on the level satisfying the requirements for organic-mineral fertilizers set up in the Regulation on executing selected provisions of the Act on Fertilising and Fertilisers (Table 3) [7]. The exception was the content of organic matter in granulate N9 (sludge to ash weight ratio as 3:7) which was 20,3%. Granulates composed only of sludge and fly ash (N9, N10, N14, N41 and N42) contained low amounts of potassium i.e. from 0,18 to 0,42 % K_2O, while the required minimum content for organic-mineral fertilizers is 1%. Therefore a decision was made to enrich the mixtures with potassium in a form easily available for plants. After KCl addition to the generic mixtures, the achieved potassium content was on the level of 8,43% for N41/m granulate and 8,83 % for N42/m granulate and was significantly higher than the required 1%. Moreover, the addition of potassium resulted in an increase of the percentage ratio of potassium to phosphorus (oxide forms) to the value of 2,4. A high percentage ratio of these elements should ensure their successive availability to plants; potassium being released faster due to its better solubility in water solution. An analysis of the data from heavy metals content determination in granulates with no potassium salt addition showed that along with an increasing contribution of sewage sludge in the dry mass of the granulate the zinc and lead content raised while the nickel content dropped. Comparing the granulates with similar share of sludge and ash but where ash was of different origin i.e. granulates N41 with N42 and N41/m with N42/m, it can be stated, that the

granulates with hard coal ash addition contained more zinc, nickel and chromium and less copper than the granulates with lignite ash addition. Copper content in granulates without potassium salt addition was in the range of 116 mg/kg d.m. (N42) to 146,37 mg/kg d.m. (N14) while in granulates enriched with potassium it was lower, amounting to the values of 82 mg/kg d.m (N42/m) and 92 mg/kg d.m (N41/m). These values were significantly lower than the permissible copper content in sewage sludge for land applications and in organic-mineral fertilisers. The content of zinc in the granulates was in the range of 1340,3 mg/ kg d.m. (N 9) - 2752 mg/kg d.m. (N14). The permissible content of 2500 mg Zn/kg d.m. for sewage sludge for agricultural applications was exceeded only in the case of granulate N14. Cadmium content in the granulates was in the range of 2,20 mg/kg d.m. - 3 mg/kg d.m. and did not exceed the permissible level of 10 mg/kg d.m specified in Regulation [6]. Granulates without potassium salt addition contained nickel in the amounts ranging from 32,2 mg/kg d.m. (N41) to 46,17 mg/kg d.m. (N9) while in granulates with potassium salt addition, nickel content was lower, on the level of 23,1 mg/kg d.m (N42/m) and 20,2 mg/kg d.m (N41/m). These values were much below the permissible content values defined for sewage sludge for land applications. Lead content in the granulates was in the range of 126,3 mg/ kg d.m. (N 9) to 207,5 mg/kg d.m. (N14). The permissible lead content of 500 mg/kg d.m. for sewage sludge used for agricultural purposes was not exceeded. The content of chromium determined in the granulates ranged from 42,4 mg/ kg d.m. (N 41/m) to 70,37 mg/kg d.m. (N10) and was below the permissible chromium content in sludge used for land applications and in organic-mineral fertilizers. Mercury in the granulates occurred in the amounts ranging from 0,95 mg/kg d.m. (N 9) to 1,71 mg/kg d.m (N 14) and did not exceed the permissible values. An overall analysis of the heavy metals content data obtained for the granulates against the permissible content values specified for sludge for different land applications in Regulation [6], shows that the granulated sludge-ash mixtures N9, N10, N41 and N42 and the two with potassium salt addition i.e. N41/m and N42/m, meet the requirements for sludge to be used for different land applications. In the case of the N14 granulate, an exceeded value of zinc content was observed for sludge used for agricultural purposes which means that it can find application for reclamation purposes of land other than agricultural i.e. for adopting the land for specific needs resulting from the waste management plans, spatial development plans or decisions on the building conditions and land management as well as cultivation of plants for composting purposes, purposes other than consumption and fodder production. A comparison of data on heavy metals content in the investigated granulates with the values specified in the Regulation on the execution of selected provisions of the Act on Fertilisers and Fertilising [7] shows that the permissible values for zinc and lead content were exceeded in all granulates except for N9 which contained the lowest amount of sewage sludge. Thus, composing sludge-ash mixtures means compromising between a product of high fertilising qualities (i.e. maximising the sewage sludge content in the mixture) that at the same time has to meet the requirements of heavy metals content specified by effective legal regulations. However, in the investigated granulates, an improvement of the fertilizing qualities occurred with an increase of the sewage sludge content in the dry mass of the mixture which in consequence caused also elevated zinc and lead amounts i.e. metals dominating in the sludge. The tests of the granulated mixtures of a selected sewage sludge and fly ash from hard coal and lignite prepared in three different proportions of these components (3:7, 1:1, 7:3), showed that the following granulates met the targeted effect of the research i.e. obtaining a product of required fertilizing qualities and heavy metals content below the permissible level for sewage sludge applications for agricultural purposes: N10 (sludge to ash ratio 1:1), N41 and N42 (sludge to ash ratio 7:3). These granulates can be considered substitutes for two-compound NP organic-mineral fertilizers. The equivalents of granulates N41 and N42 modified with potassium salt (N41/m and N42/m) contained by 30% less organic matter, nitrogen and phosphorus but higher amount of potassium (over 8% of K_2O). These granulates can be considered substitutes for three-compound NPK organic-mineral fertilizers.

IV. Summary

There are many situations in the practice of managing sewage sludge from industrial agglomerations when the heavy metals content exceeding the permissible standards becomes the main barrier in applying the stabilised sludge for agricultural purposes. One of the known and worth considering solutions to overcome this barrier is sludge mixing with fly ash – a byproduct which also finds application in agriculture e.g. as fertilisers components or for land reclamation. An additional advantage of the procedure is the opportunity to modify the chemical properties (including fertilising qualities) by selecting an appropriate proportion of the components as well as the physical and mechanical parameters by granulating the sludge-ash mixtures. In each case however, a compromise should be reached between the fertilising quality of the products and the heavy metals content so as to meet the legal requirements set up for waste used for agricultural purposes as well as to achieve a positive environmental effect. Using as an example a selected sewage sludge (with zinc content above the permissible level for sludge to be used in agriculture) and fly ash from lignite and hard coal, the authors of the presented research proved that these types of waste can be

successfully mixed in proportions 1:1 – 7:3 and granulated while meeting the permissible heavy metals levels for sludge used for agricultural purposes together with the minimum content of organic matter, nitrogen and phosphorus required for the organic-mineral fertilizers. Nevertheless, neither sewage sludge nor granulates made exclusively of sludge and ash can be considered a sufficient source of potassium for plants. The investigations showed that sludge-ash mixtures can become a complete product for soil conditioning only after their enrichment with potassium fertilizer (KCl), a source of potassium easily available for plants. According to the authors it is beneficial to apply the weight proportion of the sludge-ash mixture components as 7:3 with its simultaneous modification with potassium salt. Since the sewage sludge is a dominant component of the granulate (70% by weight), the quality of the granulates from the viewpoint of heavy metals content will depend primarily on the sludge quality. The composition of sludge from a given wastewater treatment plant, including the content of heavy metals, is subject to seasonal changes due to the volume of the influent. In order to ensure the heavy metals content on the level permitted by law, the verification should be carried out already at the stage of sewage sludge selection. Assuming that the elemental composition of the fly ash does not undergo significant changes and the ratio of sludge to ash is as 7:3, the metal content in the sludge should not be higher than (MeP-0,3MeA)/0,7 , where MeP is the permissible metal content in the dry mass of sludge and MeA is the metal content in fly ash. The procedure for handling sewage sludge, a type of organic waste which poses challenges in its management, proves that it can be successfully utilised for production of an organic-mineral means for soil conditioning not only of desired chemical properties but of appropriate physical and mechanical qualities enabling its easy transport and application.

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Table 1 : Border values of heavy metals concentrations in sewage sludge to be used in soils: effective, proposed and prospective [mg/kg d.m.]

No	Metal	Directive 86/278/EEC	Proposed	Medium-term (ca.2015)	Long-term (ca. 2025)
1	Cu	1000-1750	1000	800	600
2	Zn	2500-4000	2500	2000	1500
3	Cd	20-40	10	5	2
4	Ni	300-400	300	200	100
5	Pb	750-1200	750	500	200
6	Cr	1000-1750	1000	800	600
7	Hg	16-25	10	5	2

Table 2 : The fertilizing qualities of swage sludge and fly ash

Contents [% dry mass]	Sludge	Fly ash	
		From lignite	From hard coal
Organic substance	58,13	Not determined	Not determined
Total nitrogen	3,60	None	None
Phosphorus	2,90	0,26	0,67
Potassium	0,21	0,21	3,06

Table 3 : Heavy metals content in sludge and fly ash [mg/kg d.m.]

No.	Metal	Sludge	Fly ash from hard coal	Fly ash from lignite
1	Cu	155,7	78	96
2	Zn	3569,3	208	125
3	Cd	3,1	<2	<2
4	Ni	20,7	107	48
5	Pb	187,1	151	113
6	Cr	36,9	163	126
7	Hg	1,99	Not determined	Not determined

Table 4 : The content of organic matter and biogenes in the granulates

Granulate	Type of fly ash	Weigh ratio of d.m. sludge:ash	Organic matter	K_2O	N_{total}	P_2O_5	K_2O / P_2O_5
			%	%	%	%	-
N 9	L	3:7	20,30	0,18	1,12	2,50	0,072
N 10	L	1:1	30,67	0,22	1,30	3,05	0,072
N 14	HC	7:3	41,20	0,41	2,41	5,18	0,079
N 41	L	7:3	43,56	0,40	2,38	5,89	0,068
N 42	HC	7:3	41,83	0,42	2,32	6,09	0,069
N 41/m	L	7:3	35,73	8,43	1,70	3,62	2,33
N 42/m	HC	7:3	36,36	8,83	1,67	3,76	2,44
organic-mineral fertilisers according to Regulation [7]			at least 30	at least 1	at least 1	at least 0,5	-

L- fly ash from lignite
HC _ fly ash from hard coal

Table 5 : Total heavy metal content [mg/kg d.m.],according to the method with aqua regia, in sludge-ash granulates vs. the permissible content values set up in the Regulation on municipal sewage sludge [6] and Regulation on the execution of selected provisions of the Act on Fertilising and Fertilisers [7]

	Metal [mg/kg d.m]						
	Cu	Zn	Cd	Ni	Pb	Cr	Hg
N 9	151	1340	3,0	46,1	126	63,5	0,95
N 10	117	2044	3,0	40,2	162	70,3	1,19
N 14	146	2752	3,0	39,2	207	65,5	1,71
N 41	128	2300	2,8	32,2	180	53,2	n.d
N 42	116	2370	2,9	38,0	184	61,8	n.d
N 41/m	92	1740	2,2	20,2	139	42,4	1,23
N 42/m	82	1748	2,2	23,1	128	57,2	1,23
Permissible content according to [6]	800	2500	10	100	500	500	5
Permissible content according to [7]	400	1500	3	30	100	100	2

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2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript's Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

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Introduction:

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.
- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

Procedures (Methods and Materials):

This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic

principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

Materials:

- Explain materials individually only if the study is so complex that it saves liberty this way.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

Methods:

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

Approach:

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

What to keep away from

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently.You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.

Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.

- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.

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Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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