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A Review Article on SnO_2 based Thick Film Gas Sensors

Prof. (Dr.) G. B. Shelke

Professor and Head, Dept. of Physics, Nanasaheb Y. N. Chavan A. S. C. College, Chalisgaon
Maharashtra, India
Email –abhayshree9198@gmail.com

Abstract: *Pollution has raised its ugly head high in the global environment. It created tremendous disasters of global warming. To face such disasters is very challenging for mankind. Many gases released by vehicles and industries contribute the pollution and ultimately global warming. Gases beyond a certain limit can affect living beings. So, there is a need to detect the gaseous pollutants in the environment, even at trace levels. Many researchers are already working to detect hazardous gases in the environment and develop gas sensors at their best level. Researchers are well known about the hazards of different gases released by any means in the open environment. Still, the action has not been initiated in the desired proportion to save the environment from pollution and its hazards. Also, the researchers have the responsibility to the aware society of pollution hazards. The aim of the present study is, to well acquaint ourselves with the thick films of SnO_2 and their nanocomposite gas sensors. Gas sensors can be fabricated and developed by utilizing the pure and surface activated SnO_2 and their nanocomposites so that, they could be able to detect various gases at trace levels (ppm / ppb).*

Key Words: *SnO_2, Synthesis, Thick Films, Gas sensors, Characterizations, Polluting Gases, etc.*

1. INTRODUCTION:

The concentration of gas in the environment which produces an undesirable and disastrous change in the physical, chemical, or biological characteristics of air, soil, and water that can harmfully affect living beings is called pollution. Heavy industrialization, uncontrolled urbanization, and careless application of technology can cause pollution [1-6]. There are three major types of pollution: air pollution, water pollution, and soil pollution. Out of these, air pollution is a major threat to modern society. Current burning issues are global warming, the cruellest episodes like Bhopal gas tragedy, leakage from the Ukraine atomic reactor plant, and the blackening of world heritage places like Taj Mahal and Ajanta caves are the effects of air pollution. Along with this, some domestic threats are also occurring all over the world. The main culprits behind all such hazards are toxic, inflammable, and explosive gases. Gases play a key role in many industrial or domestic activities. In the last twenty years, the demand for gas detection and monitoring has increased. Particularly, the awareness of the need to protect the environment has grown. This century is the century of automation. It requires fast, simple, safety control and reliable measurement technology of the physical quantities.

1.1. POLLUTING GASES AND THEIR HEALTH HAZARDS:

Various gases above a certain concentration pollute the environment and can cause undesirable and disastrous effects on living beings [7-22]. The various polluting gases and their toxic effects are discussed elsewhere [17].

Over the past few decades, tin oxide-based films are widely used as gas sensors due to their high sensitivity in the presence of trace amounts of some gases of interest viz. carbon monoxide, ethanol, methane, LPG, LNG, etc. Allied to this advantage is the low cost, simple, easier, fast response and recovery, selective nature to a particular gaseous species among the mixture of gases, and the possibility of miniaturization of these devices [23-30]. The variation of the conductance measured under specific gases depends on many parameters such as intrinsic resistance, grain size [31], grain boundary barriers, detection temperature [32], etc.

Higher concentrations of gases containing sulfur led to bronchitis and lung cancer. These gases containing sulfur destroy plant cells and interfere with chlorophyll synthesis. Leaf blotching and reduction in crop yield occur even at a concentration of less than 1 ppm. Exposure of gases containing sulfur can also affect nonliving things viz. stone leprosy, increase in the rate of corrosion of metals, retardation of drying of paints, etc.

H_2S sensor model TGS 825 is already available in the market and is manufactured by Figaro Engg. Inc. Ltd. But TGS 825 is an expensive model. So, it is a need to fabricate low-cost sensors for large applicability.

H_2S is a colourless gas with the characteristic foul odour of rotten eggs. H_2S is one of the major pollutants, hazardous and toxic [27-28] in nature, which is also released from industries and laboratories. H_2S has also been liberated in volcano eruptions like natural events along with some manmade processes. So, it is a need to detect it even at very low concentrations (ppm / ppb / sub-ppb level). The aim of the present work is to develop low-cost H_2S sensors by utilizing the easily available material to a large extent and modifying the material to enhance the H_2S sensing performance. Thick films of pure and modified SnO_2 are tested and developed, which could be able to detect the H_2S at trace levels (below TLV).

1.2. APPLICATIONS OF GAS SENSORS AND THEIR NEED:

A gas sensor is a device that when exposed to the gaseous species, produces a proportional output signal corresponding to its odour, concentration, contents, etc. The gas sensor detects the odour and concentration of gases, below the detection limit of human sense organs. The output signal produced by the gas sensor may be in the form of electrical, mechanical, or magnetic in nature. Gas sensors find applications in numerous fields, viz. fire detectors, gas leakage detectors, controllers of ventilation in cars and planes, alarm devices for hazardous gases in workplaces, etc. The detection of volatile organic compounds (VOCs) or smells generated from food or household products has also become increasingly important in the food industry, in indoor air quality, and in multisensory systems. Gas sensors are popularly referred to as electronic noses.

There are many more applications of gas sensors, viz. Safety, Environmental Control, Automobiles, Food Fresheners, Medicine, etc.

Metal oxide-based solid-state gas sensors are the best selection for the development of commercial gas sensors for a wide range of applications. The great interest in industrial and domestic solid-state gas sensors comes from their versatile advantages like portable size, high sensitivity in detecting very low concentrations (ppm, ppb, or sub ppb level) of a wide range of gaseous chemical compounds, and low cost. On the other hand, traditional analytical instruments are expensive, complicated, and bulky. Solid-state chemical sensors have been widely used but they also suffer from limited measurement accuracy and problems with long-time stability. Recent advances in nanotechnology, as far as the synthesis of materials is concerned, produce novel classes of nanostructured materials with enhanced gas-sensing performance. This technology dramatically increases the performance of solid-state gas sensors. Gas sensors are needed to; minimize health hazards, avoid the hazards of global warming, avoid the cruelest episodes, and detect and control the pollutants in the environment in the form of gas or moisture.

The technological progress made by mankind has changed and shaped the world. But this progress has several side effects, the major being related to the environment. Industrial development all over the world is generating toxic solid, liquid, and gaseous wastes. Hazardous gases like CO, NO_x, H_2S, etc. are polluting the air blanket of the earth which is creating several health issues for human beings. The health issues include several diseases like respiratory tract diseases (bronchitis, asthma, nausea, shortness of breath), lung cancer, reduction in haemoglobin, impairment of the nervous system, mental retardation, disorders of the digestive system, disorders of blindness, reproductive system, hypertension, forgetfulness, headaches, etc. It has, therefore, become the need of an hour to keep watch and monitor the air quality with the help of gas sensors. Such monitoring can be made outdoors as well as indoors. The detection of gas pollution with the help of sensors can help in the elimination of these polluting gases and thus improve air quality. These gas sensors can be seen as security equipment for environmental security. The pollutant gases are of various types, and they originate in different physical conditions like temperature, radiation, etc. The sensor should work and provide accurate results irrespective of the environmental conditions where they are installed i.e., there should be no compromise in stability, selectivity, sensitivity, etc. [15].

A lot of research and development is in progress to design portable and affordable gas sensors which possess the highest response, produce ability at trace levels of gaseous species, have selective nature among the mixture of various gases, long-term stability, low cost, large applicability, etc.

1.3. PERFORMANCE MEASUREMENT OF SENSORS:

The characteristics that are desirable to measure the sensing performance of any sensor are as follows.

i) **Gas Response (S):** The gas response is defined as the ratio of the change in conductance of the sensor in the presence and absence of target gas to the conductance in absence of target gas (air). The gas response (S) is given by the relation,

$$S = \frac{G_g - G_a}{G_a}$$

Where, G_g and G_a are the conductance of sensor in air and in a target gas medium, respectively. The percentage gas response is given by the relation,

$$\% S= \frac{G_g - G_a}{G_a} x\ 100\%$$

- **ii) Selectivity:** Selectivity is defined as, the ability of a sensor to respond to certain gas in the presence of a mixture of the number of gases. Selectivity is also termed as, specificity. A good gas sensor should be very much selective for a particular gas in presence of some other gases or a mixture of gases, even at high concentrations.
- **iii) Selectivity Factor (K):** The selectivity factor of one gas over another is defined as, the ratio of the maximum response of the target gas to the maximum response of the other gas at optimum conditions, viz. temperature, gas concentration, etc.

$$K = \frac{S_{target\ gas}}{S_{gas}}$$

- **iv) Response Time (RST):** The time taken for the sensor to attain ninety percent of the maximum increase in conductance on exposure to the target gas, is known as response time.
- **v) Recovery Time (RCT):** The time taken by the sensor to get back ninety percent of the maximum conductance when the flow of gas is switched off, is known as recovery time.
- **vi) Sensitivity:** The sensitivity of a sensor is defined as the change in output of the sensor per unit change in the parameter being measured.
- **vii) Repeatability:** The ability of the sensor to produce a stable response upon the number of successive exposures of a target gas is called repeatability.
- **viii) Long-Term Stability:** The ability of the sensor to produce a stable response over a longer time span, irrespective of the number of target gas exposures is called long-term stability.
- **ix) Detection Limit:** It is the lowest concentration of the gas (ppm / ppb) that can be detected by the sensor under given conditions, particularly at a given temperature.
- **x) Resolution:** The lowest value of the difference in gas concentration (ppm / ppb), that can be distinguished by the sensor is called resolution. It is measured in ppm.
- **xi) Linearity:** It is the relative deviation of an experimentally determined calibration graph from an ideal straight line.
- **xii) Operating Temperature:** It is usually the temperature that corresponds to the maximum response to a particular gas.

2. LITERATURE REVIEW:

Jun Zhang *et al.* [33] carried out the large-scale synthesis of highly ethanol sensitive SnO_2 nanoparticles. They used a metal alkoxide hydrolysis route for the synthesis process and obtained SnO_2 nanoparticles in the range of 5 to 15 nm sizes. SnO_2 nanoparticles were characterized by transmission electron microscope (TEM), selected area electron diffraction (SAED), and X-ray diffraction (XRD). A gas sensor was fabricated from SnO_2 nanoparticles. It was applied to test ethanol as well as some other gases. High sensitivity, quick response, and good selectivity to ethanol were observed at the operating temperature of 220^{o}C.

Ansari S. G. *et al.* [34] worked on the characterization of SnO2-based sensors for different gases. A simple screen-printing technique was used for obtaining the thick films of pure SnO_2. The films were characterized for sensing H_2 and CO_2 gases using a static measurement setup. At 400 ppm, samples showed the highest sensitivity for H_2 and CO_2. Peak response was observed at 210^{o}C and 160^{o}C for CO_2 and H_2 gas respectively. They also carried out cross-sensitivity measurements.

N. Barsan *et al.* [35] developed and studied the model for interaction between CO and SnO_2 surface by the role of water vapour. They observed the presence of water vapour in the ambient atmosphere enhances the interaction between the atmospheric O_2 and SnO_2 surface. From the electronic point of view, the density of chemisorbed oxygen is increased i.e., more electrons can pass into the conduction band. Thus, the activation energy increases. This suggests that water acts as a catalyst. The operating temperature is about 600^{o}K.

S. Matsuura [36] studied new developments and applications of gas sensors in Japan. He predicted how gas sensors are needed in the modern era. Starting from the historical development and applications of gas sensors he studied the research and development of gas sensors in Japan. The newly developed sensors are given in the discussion in which energy-saving sensors, operated for an extended time of battery are the main considerations. He focused on the importance of CO_2 detectors, NO detectors, and optical gas sensors. Some commercial sensors were also discussed like Figaro Eng. Inc. and Cosmos Electric Co. Ltd. In the application area, domestic gas leak detectors, air purifiers, microwave ovens, odour checkers, alcohol checkers, and oxygen sensors are also discussed in brief.

Yasuhiro Shimizu *et al.* [37] prepared thermally stable lm- SnO_2 powders (mean pore diameter ≈ 4 nm) by employing $SnCl_2.H_2O$ as an Sn source and the self-assembly of a triblock copolymer as a surfactant to sense H_2 gas. Thick film sensors were fabricated by applying the paste of phosphoric acid large mesoporous tin oxide (PA-lm-SnO_2)

powders on alumina substrates with pair of platinum electrodes. The gas response of the sensor was measured to 1000 ppm H_2 balanced with air in a flow apparatus at 250-550ºC.

Azam Anaraki Firooz *et al.* [38] successfully carried out their research work on synthesis and gas sensing properties of nano and mesoporous MoO_3 doped SnO_2. By ultrasonic spray pyrolysis method, nano and mesoporous SnO_2 doped with and without 1-10 wt % MoO_3 powders were synthesized. Well-developed nano and mesoporous structures of SnO_2 by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy were realized. Thick films of the synthesized material were fabricated by the screen-printing technique. The gases, viz. NO_2, C_2H_5OH, and H_2 were tested at room temperature. The conclusion of the work is, doped thick films showed a high response and selectivity to 5 ppm NO_2 gas. Also, the presence of Mo species in SnO_2 lattice can improve sensor response and selectivity of NO_2 gas.

E. A. Makeeva *et al.* [39] worked on the synthesis, microstructure, and gas-sensing properties of SnO_2 / MoO_3 nanocomposites. SnO_2/ MoO_3 nanocomposites containing up to 82 mol % MoO_3 were synthesized in a broad composition range through chemical precipitation. Microstructural analysis was carried out by X-ray diffraction. The gas sensing of lower alcohols ($C_nH_{2n+1}OH$, n=1-4) was carried out by in situ conductance measurement.

M. S. Wagh *et al.* [40] successfully prepared SnO_2 thick films using RuO_2 as a surfactant for the detection of LPG. A simple, low-cost screen-printing technique was used to fabricate thick films. Response of SnO_2 by surface customized using RuO_2 was found to be larger than the responses of pure and RuO_2-doped SnO_2 to 1000 ppm LPG. The operating temperature of the modified SnO_2 sensor (300ºC) was lower than the unmodified SnO_2 sensor (350ºC). Surface customization using ruthenium as a surfactant was observed to enhance the gas response and selectivity to LPG.

L. A. Patil *et al.* [41] innovated a hetero-contact type CuO- modified SnO_2 sensor for the detection of a ppm level H_2S gas at room temperature. Thick films of pure SnO_2 by screen printing technique. By dipping process, the films were surface modified with Cu^{2+} for different intervals of time and fired at 550ºC for 24 h. The p-type CuO grains around n-type SnO_2 grains formed n-SnO2/p-CuO heterojunctions. The outcome of this innovation is that the sensor showed a very high response to H_2S gas. The response was of the order of 10^5 to 300 ppm and 10^3 to 1 ppm H_2S gas at room temperature. The sensor was highly selective to a trace amount (1 ppm) of H_2S gas from thousand times concentrations of the other toxic gases.

John S. Suehle *et al.* [42] fabricated SnO_2 gas sensor using CMOS micro-hotplates and in-situ processing. A monolithic SnO_2 gas sensor has been produced by micromachining a custom CMOS chip fabricated through the MOSIS (Metal Oxide Semiconductor Implementation Service) foundry system and then sputter depositing a SnO_2 sensing film. A maskless micromachining technique was used in realizing a micro-hotplate array structure on the CMOS chip. The sensor exhibits a fivefold conductance change in response to H_2 and O_2 exposures in a vacuum, with a response time of less than 200 S. This is a low-cost CMOS based gas sensor system. The gas sensor responses of pure SnO_2 films to H_2 and O_2 with an operating temperature of 350ºC were reported.

U. Brunsmann *et al.* [43] investigated high-resolution readout of metal oxide gas sensors using time-to-digital conversion. The method was evaluated by exposing metal oxide gas sensors to very low carbon monoxide concentrations. By combining CMOS technology with micro-electro-mechanical systems (MEMS) technology, monolithically integrated circuits with hot plates and control and measurement electronics on a single chip was presented, which detect a noise equivalent CO concentration of 30 ppb, compared with the commercially available MEMS design specified up to 50 ppb CO. the measurements were performed at 25ºC gas temperature and at a gas flow rate of 200 ml/min at a total pressure of 10^5 Pa.

Ganesh E. Patil *et al.* [44] successfully carried out the synthesis, characterization, and investigated gas sensing performance of SnO_2 thin films to H_2S gas. The SnO_2 films were synthesized by spray pyrolysis method using $SnCl_2{:}2H_2O$. The resulting SnO_2 films were characterized by X-ray diffraction and SEM. The average particle size obtained from SEM images was 56.1-68.3 nm, from XRD data, the average grain size changed from 40-56.1 nm, and from the absorption spectrum band gap values was in the range from 3.62-3.5 eV for increasing the annealing temperature from 550ºC-950ºC. The maximum sensitivity was obtained at an operating temperature of 100ºC for the exposure of 80 ppm of H_2S gas.

Liang-Dong Feng *et al.* [45] successfully prepared strontium doped SnO_2 thick film for liquefied petroleum gas (LPG) down to several ppm levels using the screen-printing technique. Characterizations were carried out by XRD, XPS and DTA-TGA analysis. The sol-gel setup for the preparation of Sr-doped tin oxide films was based on the use of stabilized solutions containing the semiconducting material precursors. In the present work sensitivity, selectivity, sintering temperature, and static and dynamic measurements were investigated. The measurements showed that the sensor exhibited high sensitivity and selectivity at 210-300ºC for domestic LPG gas.

B. Licznerski [46] developed thick-film gas microsensors based on tin oxide. The SnO_2 powders were prepared with Okazaki method, by doing some modifications in it. The powder was annealed at 600ºC and then it was mixed with an organic carrier to provide the desired rheological properties. The average size of crystallites determined by X-ray analysis was about 30 nm. The sensors were printed on 250 µm alumina substrate printed with gold electrodes to their gas sensing sides. This sensor was used to sensitize CO, C_2H_5OH, and CH_4 gases. They reported operating temperature requirements for all these gases were in the range of 400-600ºC. The study reveals the fact that the SnO_2 thick film gas sensors are suitable for the detection of explosive and toxic gases and vapours. Improvement in selectivity has been achieved due to microelectronic technology.

Jianwei Gong *et al.* [47] fabricated micromachined nanocrystalline SnO_2 chemical gas sensors for an electronic nose. SnO_2 gas sensor based on the polymeric sol-gel method has been developed to detect H_2 gas. Observed very fast response time of about 2 S, quick recovery time about 10 S and reported the operating at about 100ºC. Low power consumption, low thermally induced signal shift, and safe detection in certain environments are the salient features of this invention.

Sandipan Ray *et al.* [48] investigated the electrical and optical properties of sol-gel prepared Pd-doped SnO_2 thin films and studied the effect of multiple layers and their use as a room-temperature methane gas sensor. SnO_2 thin films of multiple layers were prepared from $SnCl_2.2H_2O$ inorganic salt by sol-gel method. A comparative study of both undoped and Pd-doped SnO_2 thin films was carried out. Electrical and Hall measurements were carried out and it has been found that undoped SnO_2 showed poor response to methane gas at room temperature. However, if the number of layers increased and if SnO_2 was doped with palladium, the increase in sensitivity was observed for methane gas at room temperature.

Smitesh D. Bakrania *et al.* [49] carried out the synthesis of SnO_2 nanoparticles by a specific type of sintered-combustion method. Fabricated the thick films of synthesized nanostructured SnO_2 material by two types of film deposition methods, viz. binder-paste method and dispersion-drop method. In both methods, materials were deposited on the alumina substrate with the use of Pt electrodes. The dispersion-drop sensors yielded excellent repeatability as compared with the binder-paste sensors. Screen printing is necessary for sensors made using the binder-paste method. On the other hand, high-quality films, in terms of structure and uniformity and resulting sensor performance, can be achieved using dispersion-drop method. Sensor performance at a fixed operating temperature of 330ºC was evaluated for CO gas in both methods.

Bee-Yu Wei *et al.* [50], fabricated a hybrid SWCNTs/SnO_2 gas sensor operating at room temperature to detect NO_2 gas by adding single-walled carbon nanotubes (SWCNTs). The technique involves giving out the heat treatment to the SWCNTs/SnO_2 layer, which was fabricated by spin coating using an organometallic solution dispersed with SWCNTs. The main purpose of utilizing SWCNTs was to improve the efficiency of SnO_2 gas sensor operable at room temperature to detect NO_2 gas. According to this study, the sensor exhibited much higher sensing sensitivity and recovery properties in detecting NO_2 gas at room temperature than the blank SnO_2 sensor.

Kamalpreet Khun Khun *et al.* [51], investigated room temperature ammonia gas sensors by SnO_2 thick films. The porous nano-sized powder has been synthesized by a simple non-aqueous sol-gel method using $SnCl_2.2H_2O$ and C_2H_5OH as precursors. Characterizations, viz. XRD, FESEM, and TEM were carried out to investigate the microstructural properties of the synthesized SnO_2 material. On average 35 nm-sized particles were found by using TEM micrographs of SnO_2 powder. Thick films by screen printing were obtained on the glass substrate. The sensing response of SnO_2 sensor towards ammonia was comparatively higher than acetone and ethanol at room temperature was reported.

Paisan Setasuwon [52], prepared SnO_2 films from sol-gel by spinning on the substrate, with various dopants, viz. Al, La, Nd, Mn, Ni, Cu, Sb, In, Pd, Pt, Nb, Si and Fe at 0.5-4 mole%. The effects of these dopants on the alcohol sensitivity of SnO_2 gas sensor were investigated. Only four dopants, Al, Pt, Pd, and Si, have shown an improvement in alcohol sensitivity. 2% Al, 1% Pt, 2% Pd and 4% Si doping increased the maximum sensitivity to alcohol at 100ºC. Si-doping seems to be highly effective.

Bienchetti M. F. *et al.* [53] reported a nanocrystalline pure SnO_2 thick film gas sensor for H_2 gas. The SnO_2 was synthesized by a precipitation method followed by calcination at different temperatures. The mean crystallite size measured by XRD was 5-6 nm. Thick films of this material on alumina substrate were obtained by the screen-printing technique. Measurements were carried out in synthetic and dry air + H_2 mixtures. A hydrogen sensor detecting mixtures from 5 ppm H_2 in the air was reported. The highest sensitivity was found at an operating temperature of 200ºC.

H. C. Wang *et al.* [54] reported fast response thin-film SnO_2 gas sensors operating at room temperature. Thin film SnO_2 gas sensor prepared by the hydrolysis and low temperature annealing of $SnCl_4$. An anti-smudge (as) prepared precursor solution was dip-coated onto a glass substrate by using the automatic dip-coating machine. The gas sensing characteristics of the thin film SnO_2 sensor were investigated by recording online the electrical response of the sensor to periodical changes between dry air (dried with silica gel) and saturated vapours of alcohols (methyl, ethyl, isopropyl, and butyl alcohol) using a simple electric circuit at room temperature. A gas sensor was obtained by heating an as-coated sensor at 150ºC in the air for 2 h. The sensor has an ultra-fast, reversible, and reproducible response to methyl alcohol vapours at room temperature. It was found that the particle size of the hydrolyzed $SnCl_4$ affects the sensitivity of the sensor.

Nguyen Van Hieu *et al.* [55] highly sensitive NH_3 gas sensor operating at room temperature based on SnO_2 / MWCNTs composite fabricated by thin film microelectronic technique. The composite thin films were prepared by using both commercially available multi-walled carbon nanotubes (MWCNTs) and nano-sized SnO_2 dispersion. Microstructural analysis was carried out by X-ray diffraction and FE-SEM. The response of this sensor strongly depends on MWCNTs content, MWCNTs diameter, thermal treatment conditions, and film thickness. The composite thin films with MWCNTs content of 15%, MWCNTs diameter of 60-100 nm, calcination temperature of 530ºC under vacuum of 10^{-2} Torr, and a film thickness of 400 nm are the optimum conditions. This sensor is found to have a very good response and recovery to NH_3 gas at room temperature.

Yong Sahm Choe *et al.* [56] achieved the patent for their work on a process for producing thin film gas sensors with dual ion beam sputtering. The present innovation provides processes for making stoichiometric, highly electrically resistant, and crystalline gas sensing layers of SnO_2 thin films for stable detection of reducing gases. It also provides processes for making stoichiometric and crystalline thin film CuO catalytic layers for the detection of dilute sulfur compound gases. The catalytic layer was made using dual ion beam sputtering, where an argon ion beam sputters targets comprising Cu or its oxides, and a pure or highly concentrated oxygen ion beam was simultaneously deposited on a substrate. The effect of the oxygen-assisted ion beam and the resulting stoichiometric, dense, and crystalline thin films are important parts of the present innovation.

P. Ivanov *et al.* [57] successfully detected ammonia and benzene via zeolite films deposited on SnO_2 / Pt-SnO_2 thick film gas sensors. Pt-doped SnO_2 covered with zeolites was used to sense CO, NH_3, C_6H_6, ethanol, and humidity at an operating temperature of 250-300ºC. Sensors were fabricated by thick film technology on an alumina substrate. Screens and pastes with different properties were used for the fabrication process. Synthesis of commercially available tin oxide material was carried out by ball mill technique. To increase the selectivity of the sensor, two different zeolite films were tested onto pure and Pt-doped SnO_2 thick film layers. EDX showed that the percentage of Pt doping was nearly 1.5% in wt. SEM analysis revealed that the particle size of tin polycrystalline oxide layers was nearly 150 nm. The gas sensing results clearly showed that a suitable zeolite layer strongly increases sensor selectivity. The results of the present work indicate the potential of zeolite-based sensors to achieve a higher selectivity in gas sensing applications.

Chi-Hwan Han *et al.* [58] developed F-doped SnO_2 by surface modification with SiO_2 and enhanced H_2-sensing properties of the sensor. F-doped SnO_2 was synthesized by the sol-gel method. Surface-modified F-doped SnO_2 with SiO_2, as well as unmodified F-doped SnO_2 microsensors, were fabricated on the silicon-based substrate with Pt electrodes and a heater. SEM photographs predict the particle size of F-doped SnO_2 was in the range of 15-30 nm. After surface chemical treatment with sodium silicate, due to slight aggregation, particle size increased up to 45 nm. The sensor was used to test the gases like H_2, CH_4, C_3H_8, and CO for the 100 to 600 ppm concentrations. A better response was observed for the F-doped SnO_2 micro sensor to H_2 gas (S=175), which was more than 40 times higher than that of the unmodified sensor (S≈4.2). The low energy-consuming sensor is a salient feature of the present work, as maximum hydrogen sensitivity was recorded at a heater voltage of 0.7 V operating at 320ºC.

Gerald Frenzer *et al.* [59] investigated gas-sensing applications by chemically synthesizing thick, porous oxide films. The method is based on the robot (Packard Multiprobe II EX) controlled application of unstable metal oxide suspensions on an array of electrodes placed on an alumina substrate. SnO_2, WO_3, ZrO_2, TiO_2, CeO_2, In_2O_3, and Bi_2O_3 were used as base materials and were optimized by doping or mixed oxide formation. Thick, porous films within the range of 10-20 µm have been developed. After exposing suitable sensor libraries containing doped base oxides with the selected set of test gases (H_2, CO, NO, NO_2) in synthetic air, the materials were evaluated for their sensor properties with the help of complex high throughput impedance spectroscopy (HT-IS). 250-400ºC was the range of temperature required to test these gases for all the mixed oxides. The study revealed that optimization in the materials to increase performance is still required.

Ching-Liang Dai *et al.* [60] achieved a nanoparticle SnO_2 gas sensor with a circuit and microheater chip fabricated using CMOS-MEMS technique. The gas sensor is composed of a polysilicon resistor and CO gas sensing film. The polysilicon resistor is the polysilicon layer of the CMOS process. SnO_2 was prepared by the sol-gel method. The micro heater was used to provide a working temperature of the gas sensor. When adsorbs the CO gas, the gas sensor changes its resistance. An amplifier circuit is used to convert the resistance of the sensor into the voltage output. The experimental result showed that the sensitivity of the CO gas sensor is about 1 mV/ppm.

Frank Rettig *et al.* [61] presented their investigation on direct thermoelectric hydrocarbon gas sensors based on SnO_2. The design of the direct thermoelectric gas sensing device was optimized with respect to low internal film resistances. SnO_2 material has been used in the present investigation. The film thickness of this material was about 20-

40 µm, achieved with the help of the screen-printing process. The sensor showed a very reproducible behaviour with an internal resistance of about 0.5 MΩ at 400ºC. The repeatability and reproducibility of thermoelectric gas sensors with an adapted design were also compared to the conductometric gas sensors. The operating temperature for sensing hydrocarbons using this thermoelectric gas sensor was about 400ºC.

Jing Wang *et al.* [62] successfully fabricated a formaldehyde (CHOH) gas sensor with a composite of nanostructured tin oxide and functionalized multi-wall carbon nanotubes (MWCNTs). The sensitivity of the composite SnO_2/MWCNTs to formaldehyde gas was much improved using this technique than the techniques which were innovated earlier. Formaldehyde is harmful to human eyes, nose, etc. Other gases, viz. acetone, and toluene were also tested by this sensor. The report reveals that formaldehyde showed higher sensitivity among all of them.

Il Jin Kim *et al.* [63] invented indium-doped nanocrystalline micro semiconductor tin oxide gas sensors to detect carbon monoxide gas. The precursors of SnO_2 nanocrystalline powders doped with In_2O_3 were prepared by the sol-precipitation method. The precursors were calcined at temperatures from 200 - 900ºC in the air for 2 h to produce SnO_2 and In_2O_3/SnO_2 nanocrystalline rutile powders with different average particle sizes. A high-performance CO sensor based on a simple device utilizing SnO_2 or In_2O_3/SnO_2 nanocrystalline material with PdO_x was fabricated. The sensor showed a high response and good sensitivity to CO at an operating temperature of 200ºC. The response time was 8 S and the recovery time was less than 10 s in presence of 50 ppm CO gas.

Sardar M. Ayub Durrani [64] obtained thin films of tin oxide by electron beam evaporation method. The thickness of the films was in the range of 220-400 nm. The effects of the sensor biasing voltage and film thickness on the CO sensing of SnO2 thin films were investigated. The current-voltage resistance characteristics of the sensor in the air have shown the formation of Schottky barrier at the metal-semiconductor interface. The maximum sensitivity was obtained at an operating temperature of 350ºC. It was also reported that; the sensitivity of the films strongly depends on sensor biasing voltages and thickness of the films. Maximum sensitivity was observed at lower biasing voltages and higher thicknesses of the films.

Matthias Batzill [65] carried out the review on surface science studies of SnO_2 gas sensing material. This study gives an overview of how surface science studies can contribute to a fundamental understanding of metal oxide gas sensors. The tin oxide was used as a specimen system for metal oxide gas sensor materials surface science studies of single crystal SnO_2 have been reviewed. The composition, structure, and electronic and chemical properties of (110) and (101) surfaces were discussed. Finally, it was concluded that the chemical and gas-sensing properties of the materials strongly depend on the surface composition.

Jung Y. Kim *et al.* [66] designed a smart gas sensor system for room air cleaners of automobiles using thick film metal oxide semiconductor gas sensors. Selected the semiconductor gas sensors with different ranks (sensor resistances) from Figaro Eng. Inc., Japan. Using the thick-film technique, the sensor material (metal oxide semiconductor) was printed on suitable electrodes which were printed on the alumina substrates. The main sensing material used was the like SnO_2. The sensor is used to recognize the air quality of the passenger space of automobiles.

Xing Jianping *et al.* [67] obtained the metal oxide SnO_2, ZnO thin film sensors by a powder sputtering technique. According to their study, this method is likely to become popular in the field of gas sensors. The main procedure was depositing the gas sensing layer by powder sputtered method with steady doping. ZnO thin film is another gas-sensing material that can be developed besides SnO_2. The gases under test were CO, C_2H_5OH, and gasoline with the operating temperature ranging from 260-370ºC.

Akira Fujimoto *et al.* [68] proposed a method to distinguish smells using a SnO_2 gas sensor. A commercially available conventional gas sensor was used. The sample gases used were alcoholic gases. Four carboxylic gases were also used to compare with alcoholic gases. A simple electrical circuit was used to measure the response of SnO_2 gas sensor. The sensor was operated under heater modulation with triangular and rectangular pulse currents to distinguish smells. Four kinds of alcoholic gases have different delay outputs. These results showed that a smell-distinguishable system can be realized using SnO_2 gas sensor.

J. K. Srivastava *et al.* [69] studied CuO-Doped SnO2-based thick film gas sensors for the detection of H_2S gas. This review focuses on commercial and experimental gas sensors that uses metal oxide semiconductors.

R. S. Pandav *et al.* [70] investigated nanocrystalline manganese substituted nickel ferrite thick films as ppm-level H_2S gas sensors. The nanocrystalline manganese substituted nickel ferrite dry powders were synthesized by a simple sol-gel auto-combustion technique.

Thixotropic pastes of as prepared ferrite powders were formulated, and screen printed on glass substrates to form thick films, followed by firing at 450ºC. The characterizations were carried out by XRD, SEM, TEM, etc. The gas sensing behaviour of the samples was characterized by exposing the films to various inflammable and toxic. A sensor having an equivalent amount of Fe and Mn ions (x =1) exhibits high selectivity and the most sensitivity towards 20 ppm of H_2S

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gas at 350°C. The effect of operating temperature, gas concentration, type of gases, etc. on gas response were studied and discussed.

G. B. Shelke *et al.* [71] carried out the work on the synthesis, characterizations, and gas sensing performance of $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite material. The material was prepared by using synthesized ZrO_2 and SnO_2 powders by taking their 1:1 proportion. Thick films of nanostructured pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder were fabricated by the screen printing technique. These films were surface functionalized by SrO_2. The surface morphology, chemical composition, and the crystal structure has been investigated by FESEM, EDAX, XRD, etc. Electrical and H_2S gas sensing performance of the thick films were also studied along with other parameters, viz. Response, recovery time, and the long-term stable nature.

G. B. Shelke *et al.* [72] studied the surface functionalized $Zr_{(0.75)}Sn_{(0.25)}O_4$ by SrO_2 thick films as H_2S gas sensors. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film was almost less sensitive to H_2S. Among various additives tested, SrO_2 in $Zr_{(0.75)}Sn_{(0.25)}O_4$ is outstanding in promoting H_2S sensing. Surface modification by activation is one of the most suitable methods of modifying the surface of thick films. The sensor has good selectivity to 5 ppm H_2S gas against LPG, NH_3, O_2, CO_2, Cl_2, H_2, and C_2H_5OH at room temperature.

3. MATERIAL SYNTHESIS AND THICK FILM FABRICATION:

Tin is principally found in the ore cassiterite (tin oxide). It is obtained commercially by reducing the ore with coal in a furnace. SnO_2 is a wide band gap semiconducting oxide having an energy gap of 3.6 eV. It crystallizes in the rutile structure. Its unit cell contains two tin and four oxygen atoms. It has tetragonal symmetry. Each tin atom is surrounded by a distorted octahedron of six oxygen atoms and each oxygen atom has three tin nearest neighbors at the corners of an almost equilateral triangle. SnO_2 is used as a polishing powder and is sometimes known as putty powder. Tin oxide is used for ceramics and gas sensors. In gas sensors, the sensor area is heated to a constant temperature (a few hundred degrees Celsius), and in the presence of a test gas, the electrical resistivity drops. SnO_2 wires are commonly used as the detecting element in carbon monoxide detectors [15].

Fig. 1 (a): Disc type ultrasonicator

Fig. 1 (b): Microwave treatment following the centrifuge technique

Fig. 1 (a) shows disc type ultrasonicator and Fig. 1 (b) shows microwave treatment following the centrifuge technique. Nanostructured SnO_2 powder was synthesized by disc-type ultrasonicated microwave treatment followed by centrifuge technique [71,72], by hydrolysis of AR grade tin oxychloride in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol in the ratio of 1:1. This solution was then mixed with 1M aqueous solution of tin oxychloride in the ratio 1:1. The special arrangement was made to add dropwise aqueous ammonia (0.1 ml / min.) with constant stirring until the optimum pH of the solution becomes 7.9. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. Then the precipitate was allowed for ultrasonication and then kept in a microwave oven for 10 minutes with continuous on-off cycles, periodically, followed by calcination at 500°C for 2 hrs in a muffle furnace. The dried precipitate was ground by agate pestle-mortar to ensure sufficiently fine particle size and recalcined in a muffle furnace at 500°C for 2 hrs, to eliminate the organic impurities, if present. Thus, the dry white powder of nanostructured SnO_2 has been prepared to use.

3.1 THICK FILM FABRICATION TECHNIQUE:

The use of thick film technology in the production of chemical sensors has opened up the possibility of manufacturing sensors in a cost-effective manner. Such properties of a thick film sensor are highly desirable for chemical applications. Furthermore, thick film technology can produce sensors from nano-scaled materials. This is an advantage because a minute sample volume is required. Also, the portability of the interface instrument for the sensor can be realized.

Thick film technology based on glass and ceramic compositions is very stable in severe conditions such as high temperatures or corrosive environments. Deposition of the layers is mostly carried out by using screen printing for high-volume and low-cost production. Each layer is printed with a paste comprising a functional material and a temporary organic vehicle. After deposition, the solvent was removed by drying followed by firing, to eliminate the organic binder and sinter the materials. Glass frits are commonly used alone for over-glazes and as a permanent binder in thick film technology. Commonly ceramic substrates made of mostly alumina (Al_2O_3), silicon, glass-ceramic, and sapphire with appropriate surface finish are used. The change in resistance for thicker films is large as compared to thinner ones. Thick film technology involves screen printing methodology and thick film fabrication.

Screen-printing is a simple method that allows the production of low-cost and robust oxide thick film sensors with good reproducibility, provided that, the starting materials are well controlled. It involves printing the thixotropic paste through a mesh screen which defines the desired pattern on the substrate. The thixotropic paste of the semiconducting material contains finely divided particles of basic sensor material and additives along with organic binders, whereas the substrate is usually made up of ceramic, steel, glass, etc. The sensor material has a relatively high viscosity but when forced through the screen mesh by the squeegee blade, the paste undergoes sheer thinning which allows it to penetrate through the screen mesh which defines the desired pattern on the substrate. Upon contact with the substrate, the sensor material returns to its viscous state forming the desired pattern. The pattern thus formed using screen printing technology have a thickness that ranges from 30 to 40 µm and is thicker than those obtained by other printing techniques. Thus, printing such films using screen printing is called, 'Thick Film Technology'.

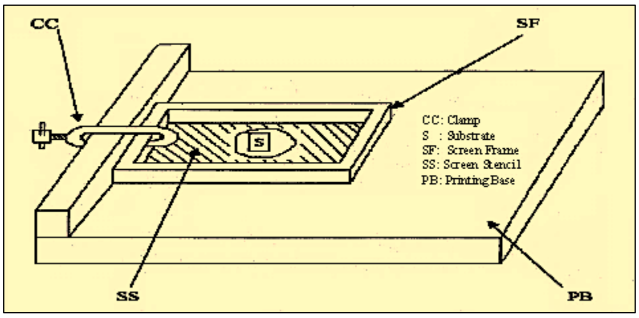

Fig. 2: Screen-printing set-up board

As shown in Fig. 2, the screen-printing setup contains a screen base, frame, stencil, squeegee, and substrate. The screen stencil is made up of a fine mesh of polyester, and nylon material which is stretched and mounted on preferably a wooden frame. The photosensitive emulsion is spread over the mesh and with the help of the photographic method, the desired pattern is obtained. The squeegee is a flexible polyurethane blade (sometimes neoprene) held in a rigid mount or handle. It is used to spread the thixotropic paste evenly over the screen so that the paste oozes down through the pores (open areas) of the screen mesh onto the substrate. A detailed procedure was adopted for making stencil, cleaning the substrates, and screen printing [71,72].

Stencil preparation and cleaning of the substrates:

- A four times larger piece of chromline film (than the required pattern to be developed) was taken.
- This piece was pasted with a solution comprising of thick film coating lotion and sensitizer mixed in the ratio 20:1.
- The chromline film was allowed to dry and remove the protective layer on the top of chromline film.
- The mask was placed with the required pattern in contact with chromline film and exposed to solar radiation for an appropriate time interval (~ 2 min.).
- The screen was washed in a water bath and the portion which was not exposed to light dissolved in water.
- The windows for sensor patterns are ready to print.
- The substrates were kept in chromic acid for 15 min.
- The substrates were washed thoroughly in water to remove the acid.
- The washed substrates were immersed in a soap solution for 5 min.
- Substrates were finally cleaned in an ultrasonic cleaner and dried under an IR lamp for 30 min.

These samples are then subjected to a temperature in the range of 70-130°C for drying under an IR lamp. Curing is done to avoid the blistering of the film. It has two steps: removal of organic binder and high-temperature curing / firing. In the first step, the residues of the organic binder (even after the drying process) are eliminated by heating at a low temperature. In the second step, the film is subjected to a furnace under controlled conditions. The chemical reactions that take place, give the required electrical and physical properties of the film.

3.2 STATIC GAS SENSING SYSTEM:

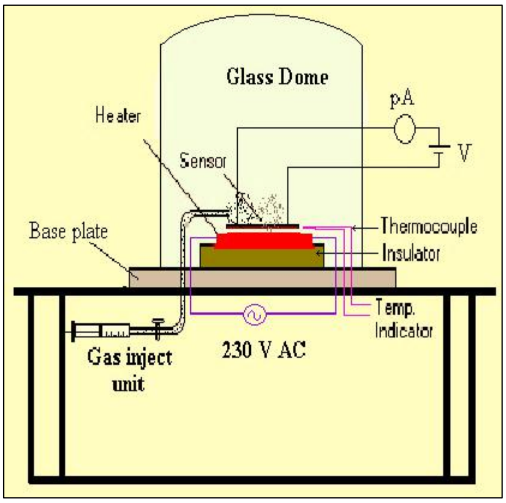

Fig. 3: Block diagram of static gas sensing system

Fig. 3 shows the block diagram of the static gas sensing system. The sensor element, heating unit, dc power supply, gas inject unit, temperature measuring unit, current meter (pico-ammeter), glass dome, and steel base plate are the major components of a static gas sensing system. The heating unit is fixed on the base plate. It provides the desired temperature to the sensor for its proper performance. The sensor sample to be tested was mounted above the heater. Cr-Al thermocouple is mounted to measure the temperature. The output of the thermocouple is connected to the temperature indicator. An inlet gas port was fitted at one of the ports of the base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas by a gas inject syringe. 0-30 V d. c. is applied to the sensor element constantly for measurement of I-V characteristics and 30 V d. c. for gas sensing and the current is measured by pico-ammeter [71,72].

4. CONCLUSIONS:

A review of the existing literature suggests that the modified and unmodified SnO_2 thick films possess several important areas of applications of modern microelectronic techniques, because of their uses in the production of advanced infrared detectors and sensors for sensing toxic gases. The parameters, on which the performance of the gas sensor depends, can be optimized for better performance of the sensor. Operating temperature, additive concentration (doping concentration in wt % and dipping time), calcination temperature, etc. are the parameters of the sensor to be optimized. The review also reveals that many researchers studied SnO_2 thick films. Also, very few attempts have been made to study the dipping time variation with the response of gas. Hence, it is the need to study the effect on structural, electrical, and gas sensing properties by changing dipping time. There is a great space to work for the development of SnO2-based gas sensors.

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Authored by

K. B. BENDRE

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Nanasaheb Y.N. Chavan Arts, Sci & Com College, Chalisgaon.

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SILAGE PREPERATION USING LEGUMINOUS AND NON -LEGUMINOUS FORAGES

K. B. BENDRE
Nanasaheb Y.N. Chavan Arts, Sci& Com College, Chalisgaon 424101

Abstract:-
The most commonly used silage crops are non-leguminous which includes maize, *Sorghum*, sudangrass, bajra, hybirdnapier etc. Out of these all maize and *Sorghum* are supposed to be best. So far as leguminous crops are concerned lucerne, berseen and cowpea are not suitable But after giving some treatments they may also be converted into good quality silage Non leguminous forage crops can be mixed with leguminous forage for making silage of good quality.

Silage are made from forages of bajra, cowpea, *Dolichos*and the mixture of bajra with either cowpea or *Dolichos* and the mixture of *Sorghum* + *Dolichos* and maize + *Dolichos*. The crop material either with a single or two crops was chopped and silage were made. All silage samples contained other nutrients except calcium (Ca), in appreciable quantity for animal feeding. The overall results suggested that on the basis of pH values silages were not perfect and demanded need of silage additive before ensiling.

Keywords - silage, leguminous, non-leguminous, forage.

Introduction :-

The most practical solution lies in conserving supplies of green fodder available during flush season either as hay or silage, so as to use it during scarcity period. Silage is good method for conservation of green fodder, wherein the crop nutrients are preserved properly and offer a nutritious and palatable feed to cattle. (Kumar et al ,2014 ,Balwindarkumar et al ,2019).

Practically any crop having sufficient soluble carbohydrates and moisture to produce the desired quantities of acids may be made into silage. The most commonly used silage crops are among graminaceous crops, maize, *Sorghum,*sudangrass, bajra, hybrid napier etc. Out of all maize and sorghum are supposed to be the best crops for silage making. So far leguminous crops are concerned lucerne, berseem and cowpea are hot suitable for silage making but after giving some treatments they may also be converted into good quality silage. For preserving leguminous crops which have less percentage of sugar, the fodder is sprinkled with a solution of molasses in water at every one third meter of filling to provide the necessary amount of sugar for silage making graminaceous forage crops can be mixed with leguminous forage for making silage of good quality (Sohane and Choudhary, 2001)

Materials and Methods

To obtained green foliages, the crops viz maize, bajra, cowpea, and *Dolichos* were cultivated on the fields of "Maharashtra Shell vaMendhiVikasPrashetral,",Bilakhed , as per recommendation of Mahatma PhuleKrishiVidyapeeth, Rahuri. The foliage were harvested at pre flowering stage with a steel cutter and immediately brought into the laboratory. The vegetation was chopped into 2-3 cm. pieces and used for preparation of silage, Bajra, cowpea, *Dolichos* (dhorwad) and the mixture of these crops; along with *Dolichos* mixed with maize and *Sorghum*.

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The chopped material was placed in plastic containers (18.5 x 10cm) and pressed to make it compact and exclude air. The container was capped and sealed with wax. These made the container air tight to maintain anaerobic condition for ensilged material. The container or 'laboratory silos' were left at room temperature in dark until used.

After 45 days, the boxes were opened and physical characteristics i.e. colour, texture odour etc. of resulting silages were examined. A sample of fresh silage was taken for the determination of pH, buffering capacity (BC), titratable acidity (TA), total volatile fatty acids (TVFA) and lactic acid (LA). An another sample of silage was dried in an electric oven, initially at 95 ± 5°C till constant weight/ The dry sample were ground to a fine powder and used for subsequent analysis.

Dry matter and moisture content in the samples were measured by considering loss in weight during drying . For determination of remaining constituents dry samples were used. For the measurement of water soluble reducing sugars (WSRS) in terms of glucose using Folin -Wu tubes (Oser, 1979). The N Content was determined by microKjeldahl method and CP was expressed as N x 6.25. A.O.A.C. 1970) methods were followed for the estimation of crude fat (Ether Extract) ash, acid insoluble ash (AIA), Nitrogen free extract (NFE}, total carbohydrate (TC) and calcium (CA) along with crude fibre (CF), Phosphorous (p) using recommended standard methods. All the samples were analyzed in triplicate.

Results and Discussions :-

In present experiment, silage were made from foliage's of bajra, cowpea *Dolichos*(Dhorwal) and the mixt ıre of bajra with either cowpea or *Dolichos* and mixture of *Sorghum* + *Dolichos* and maize + *Dolichos.* In mixture the two crops were taken in equal proportion. The crop material eitl er with a single or two crops were chopped and silages were made. The moisture content in chopped material ranged from 73.50 to 79%. In general, the crop with low moisture content is desirable character for silage making (Mungikar and Joshi , 1976). Silage made from chopped material had higher value for T.A. (61.3 to 78.6) indicating acid fermentation, whereas, silage made from mixtures showed lower vanes for TA (37 to 72) and thus showed decreased silage fermentation. A variation in TA was observed due to nature of the ensiled material.

The buffering capacity (BC) varied widely however, the variation was noticeable. Silage made from bajra had lower BC than the two leguminous crops, the low BC in case of bajra may be due to low protein content in it; as also pointed out by Reddy and Mungikar (1987) and Basole (1994). In all silage samples,pH was higher than 4.00 ; it was as high as 5.75 in cowpea. Mc Donald and Henderson (1962) suggested that a good silage has pH within the range of 3.8 to 4.2. In view of this, looking at pH values, all silage samples were not up to the mark, which might be due to low lactic acid production and high buffering capacity. There was considerable variation in the contents of TWA which ranged from 6.6 to 10.2 (Table-1). In general silage from mixture of bajra cowpea have higher value for TVFA. The water soluble reducing sugar content ranged between 0.84% to 2.08% depending on crop species.

The dry matter (DM) content in *Dolichos*(Dhorwal) was high among all of the crops. The legumes were with higher values for protein content, which ranged between 10.1 to 15,6 indicating suitability of chopped and ensiled materials in animal nutrition. The CF varied within a wide limits of 24,3 to 34%. All silage samples contained other nutrients except calcium (Ca), in appreciable quantity for animal feeding. The overall results suggested that on the basis of pH values, silages were not perfect and demanded need of silage additive before ensiling .

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Table -1

Chemical Composition of silages made from chopped foliages of Bajra, Cowpea,*Dolichos* and Mixtures.

Crop(s)	Moisture (%)	Titratable acidity m.equiv/ 100gmDM	Buffering Capacity m.equiv/ 100gmDM	pH	Lactic acid (% of DM)	Total viability fatty acid (TVFA) mM/100gm	Water soluble reducing sugar (% of DM)
Bajra	79.0	78.6	17.2	4.36	4.02	6.8	2.08
Cowpea	78.0	76.8	33.0	5.75	2.80	9.6	1.10
Dolichos	73.5	61.3	55.4	4.65	2.38	10.2	0.93
Bajra + Cowpea	79.0	72.0	34.0	5.00	3.05	8.3	0.84
Bajra + *Dolichos*	76.4	68.4	44.2	4.45	3.10	8.1	1.12
Sorghum + *Dolichos*	78.3	47.2	30.6	4.05	3.80	6.6	1.45
Maize + *Dolichos*	77.0	37.0	28.3	4.10	3.64	7.4	2.00

Table -2

Nutrient Content of silages made from chopped foliages of Bajra, Cowpea, *Dolichos* and Mixtures.

Crop(s)	% dry matter DM	% of dry matter (DM)								
		Crude Protein (CP)	Crude Fibre (CF)	Ether extract (EE)	Ash	ASA	NFE	TC	Ca	P
Bajra	21.0	10.1	24.3	8.20	12.30	11.75	45.1	69.4	1.14	0.37
Cowpea	22.0	15.6	34.0	2.31	9.60	8.12	38.5	72.5	1.69	0.30
Dolichos	26.5	13.8	31.9	2.00	10.10	8.87	42.2	74.1	1.85	0.29
Bajra + Cowpea	21.0	13.4	29.2	4.90	10.80	9.24	41.7	70.9	1.27	0.34
Bajra + *Dolichos*	23.6	11.8	26.7	5.30	11.00	9.38	45.2	71.9	1.41	0.31
Sorghum + *Dolichos*	21.7	11.4	29.6	5.40	9.94	8.17	43.6	73.2	1.22	0.33
Maize + *Dolichos*	23.0	10.9	29.7	6.10	10.30	8.90	43.0	72.7	1.27	0.36

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02

PREPARATION OF HAY USING GREEN FOLIAGES OF BAJRA CV. RAJCO

Dr. K.B.Bendre
Nanasaheb Y.N.Chavan
ASC College,Chalisgaon.(MS)

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Abstract :-

The objective behind making hay and silage is to preserve forage resources for the dry season or winter to ensure continuous regular feed for livestock either to sustain growth fattening or milk production or to continue production in difficult periods when market prices are highest.

Hay making is easy and every farmer can easily adapt the technique. The only thing to keep in mind is the proper time of cutting, stages of cutting, and the size of chalf fodder. The present study deals with the hay prepared from the Green foliage of Bajra Cv.Rajco bajra.

The principle of hay making is to preserve the nutritional value of forages by drying it to a level at which the activity of microbial decomposers is inhibited. The moisture content of 10-12% is the optimum level for halting the microbial activity (Balwinder Kumar et al. 2019). To mitigate the problem of animal feed shortage during the lean period, the conservation of forage appears to be the only alternative. Bajra Cv.Rajco bajra resulted in good hay with 81.9 % dry matter and 4.4 % relative water content (RWC) when dried in Sun for 6 days.

Keywords:- Hay, Rajco bajra, Conservation, Green foliages.

Introduction:-

Bajra is good for hay and silage making , bajra is ready for fodder harvest in 50-55 days and produces green fodder to the tune of 30 t/ ha. Pearl millet is the fourth most important grain crop next to rice,wheat and sorghum. The crop is cultivated for grain as well as fodder in semi-arid and tropical region of Africa and Asia including India. It is a quick growing , disease resistant, high tillering fodder crop. It can be sown early in spring under irrigated condition and in kharif under rainfed condition.it is not suitable in high rainfall areas It does well even on light soils.

India is an agriculture country with a large livestock population making dairy and livestock industry and important subsidiary occupation of farmers. It boosts economy of the country by providing milk, meat, wool, etc. India has recently emerged as the largest producer of milk in the world though livestock productivity is very low as compared to the developed countries. The low productivity of the animals is chiefly due to an improper supply of nutrients. Poor supply of nutrients to livestock during the scarcity period is a matter of concern. Both quantitatively and qualitatively supply of feed nutrients which is further compounded during the lean and scarcity period (Singh and Mujumdar 1992; ; Kumar et al. 2014). Inadequate supply of quality fodder has been identified as one of the reasons for poor livestock productivity (Anjum et al 2012; Kumar et al 2016).

The objective behind making hay and silage is to preserve forage resources for the dry season or winter to ensure continuous regular feed for livestock either to sustain growth fattening or milk production or to continue production in difficult periods when market prices are highest. The present study deals with the hay prepared from the Green foliage of Bajra Cv.Rajco bajra.

Materials and methods:-

Green fodder of bajra (Pennisetum Americanum (L) Leek) (Syn P. typhoideum cultivar Rajco) was used for hay making. The crop was harvested early in the morning at pre-flowering stage and batches of 1.5kg green foliages where dried in different conditions that are in an oven, under the sun, or in shade with or without cover with or without turnings.

The batches of green foliage were kept for drying under given conditions in the sun, the weight of the individual batches was recorded at the same time on a subsequent day till constant weight.

The dry matter content in the foliage was a calculated with the figures obtained for oven-dried samples. To assess water loss from the sample relative water content (RWC) was calculated as described by Harris and Thaine (1975) using the following equation-

$$RWC(\%) = \frac{Wt - Wd}{Ws - Wd} \times 100$$

There Wt is the sample weight at time t, Ws is the saturation or initial weight and Wd is dry Weight.

Results and discussion:-

The crop selected for this investigation resulted in good hay after drying. Based on colour, it was observed that when the sample was dried in an oven, it gives off its green colour resulting in pale green to grey hay. The sample, which was covered with polythene paper, resulted in bad products with yellow colour and undesirable odor. This was probably due to the fementation process which took place under an anaerobic condition created by polythene. The pH of the polythene sample was 4.1 indicating acid fermentation. The paper cover was better than the polythene cover as the sample could retain its colour, however, the rate of drying was poor. The sample, which was dried in shade resulted in green hay particularly when frequent turnover was given; the fodder dried in sun made hay in less time but the resulting hay was not as green as that resulted from shade drying.

Table 1 gives an account of the drying rate of fodder species selected for hay making under different conditions. The table gives information on the decrease in weight and relative water content of the fodders under oven, sun, and shade drying. The table also provides information on percent dry matter of resulting hay. Green fodder of Rajco variety of Bajra resulted in good hay with 81.9% dry matter and 4.4 % relative water content (RWC) when dried in sun for 6 days.

Statistical studies show that there was a maximum average 0decrease in weight in Bajra (828 gm) . However, the variation in a decrease in weight was more in Oven drying (83.1) than in shade drying (56.3) as indicated by the value of the coefficient of variation (CV).

Table 1: Drying rates of Bajra (Cv. Rajco) under various conditions

Duration from 10th January 2019 to 16th January 2019

Crop and Cultivar	Drying period (days)	Method of drying									
		Oven (60 °C)		Sun Drying		Turnover		Shade Drying		Turnover	
		Weight (g)	RWC (%)	Weight (g)	RWC (%)	Weight (g)	RWC (%)	Weight (g)	RWC (%)	Weight (g)	RWC (%)
Bajra (Rajco)	0	1500	100	1500	100	1500	100	1500	100	1500	100
	1	570	23.8	980	58.4	1000	60.6	1070	63.8	1090	67.2
	2	280	2.4	760	40.8	780	50.4	820	49.8	840	47.2
	3	250	0	640	31.2	670	33.6	700	36.0	730	38.4
	4			530	22.4	580	25.4	590	24.0	610	30.4
	5			420	13.6	470	17.8	520	21.6	540	23.2
	6			305	4.4	340	7.2	433	14.8	470	17.6
	% DM of hay	100		81.9		73.5		57.5		53.2	
	Mean	650		733		763		806		828	
	SD	527.4		417.5		409.5		406		392	
	CV (%)	83.1		65.3		62.6		61.3		56.3	

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65

Types of Functional English Syllabi and Their Utility in the Indian Context with a Special Focus on Notional Functional Syllabus

Dr. Vijay Shirsath,
Assistant Professor & Head
Dept. of English
Nanasaheb Y. N. Chavan Arts, Science and Commerce College, Chalisgaon.

Abstract:

The present paper explores the various functional English syllabi. It assesses their relevance and effectiveness in the Indian educational sector. However, central to this discussion is the Notional-Functional Syllabus which has originated from the 'communicative movement in language teaching', which emphasizes semantic and communicative dimensions over traditional grammatical structures. This analysis extends to diverse syllabi forms, including Functional, Negotiated, Natural, Subject-matter, and Task-based, to understand their distinctive features and applicability in Indian educational settings.

Introduction

The evolution of language teaching methodologies has ushered in the functional view of language, conceptualizing it as a tool for "functional meaning expression" (Richards & Rodgers, 21). This approach, emphasizing semantic and communicative aspects, marks a shift from traditional grammar-centric methods. In the Indian context, where English serves as an essential second language and a medium of instruction, assessing the efficacy of various functional syllabi is crucial.

1. The Notional-Functional Syllabus

The Notional-Functional Syllabus was first introduced by Wilkins in "Notional Syllabuses" (1976).It is a cornerstone in Communicative Language Teaching (CLT). It focuses on the "meaning systems underlying communicative language use, rather than conventional grammar and vocabulary" (Wilkins, 1976). This syllabus encompasses semantic grammatical categories like "frequency, motion, location, and communicative functions like requests and complaints" (Richards & Rodgers, 21). Despite its innovation, critics like

Widowson argue that it only partially addresses semantic and pragmatic rules, underscoring the need for a discourse-centered approach.

2. Communicative Syllabus Variants

Yalden (1987) categorizes communicative syllabi into five types:

2.1 The Functional Syllabus

Proposed by linguists like Austin, Wilkins, and Jones, this syllabus advocates for a focus on functions and notions over grammar. It covers language functions (e.g., requesting), notions (e.g., 'time'), rhetorical skills, and linguistic forms (Kale, 24). Its emphasis on social purposes and linguistic accuracy aligns well with real-life language use.

2.2 The Negotiated Syllabus

This syllabus promotes learner autonomy, placing greater emphasis on the learner than the teacher. It allows learners to directly interact with syllabus designers, fostering "an interactive learner-centric environment" (Kale, 24).

2.3 The Natural Syllabus

Based on Terrell's 'Natural Approach,' this syllabus is designed for beginners, focusing on "developing basic communication skills in oral and written forms" (Krashen& Terrell, 185).

2.4 The Subject-matter Syllabus

Applied in Canadian immersion teaching, this approach integrates subject matter teaching in the target language, thus "enhancing language learning through content exposure" (Kale, 25).

2.5 The Task-based Syllabus

Also known as the 'procedural approach,' it emphasizes task performance over language structure. Influenced by Prabhu's Bangalore Project, "it prioritizes comprehensible input and task accomplishment in language teaching" (Johnson & Johnson).

3. Utility in the Indian Context

In India, where English is a vital second language, the choice of an appropriate syllabus is influenced by factors such as learner proficiency, educational objectives, and contextual needs.

3.1 Functional Syllabus in India

The Functional syllabus, with its practical focus on real-life language application, is highly pertinent for Indian learners. It equips them to utilize English in diverse social and professional settings. This syllabus's emphasis on social interactions and linguistic accuracy aligns with the communicative needs of Indian students, who often use English as a tool in multinational corporations, higher education, and international communications.

3.2 The Negotiated and Natural Syllabi

The Negotiated syllabus, fostering learner autonomy, can be particularly effective in adult education and professional training programs in India, where learners often have clear goals and specific language requirements. In contrast, the Natural syllabus is ideal for beginners and school-level students, gradually building their language skills in a stress-free, acquisition-focused environment.

3.3 Subject-matter and Task-based Syllabi

The Subject-matter syllabus is particularly relevant in Indian bilingual education settings, where content learning and language acquisition go hand in hand. It allows for immersive learning, where students learn English through various subjects. The Task-based syllabus aligns well with India's growing focus on skill-based education, enabling students to learn English through practical tasks and real-life scenarios, thus making language learning more engaging and relevant.

3.4 Regional Diversity and Linguistic Plurality

India's linguistic diversity necessitates syllabi that can be adaptable across different linguistic backgrounds. The Functional and Task-based syllabi, with their flexibility and focus on practical language use, can be more effectively tailored to meet the needs of learners from varied linguistic backgrounds.

3.5 Challenges and Opportunities

Implementing these syllabi in India also presents challenges, such as the need for trained educators, resources, and a shift from traditional rote-learning methods. However, the potential benefits, including enhanced English proficiency and better preparation for global communication, present significant opportunities for educational advancement.

Conclusion

The adoption of Functional English syllabi in India offers a pathway to more effective and practical language education. A combination of these syllabi can cater to the diverse needs of Indian learners, fostering efficient communication skills in English. Syllabus selection should be driven by learners' requirements, educational settings, and specific goals of the English language program, recognizing the unique linguistic landscape of India.

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Authored by

Dr. Vijay Shirsath, Assistant Professor & Head

From

Nanasaheb Y. N. Chavan Arts, Science and Commerce College, Chalisgaon.

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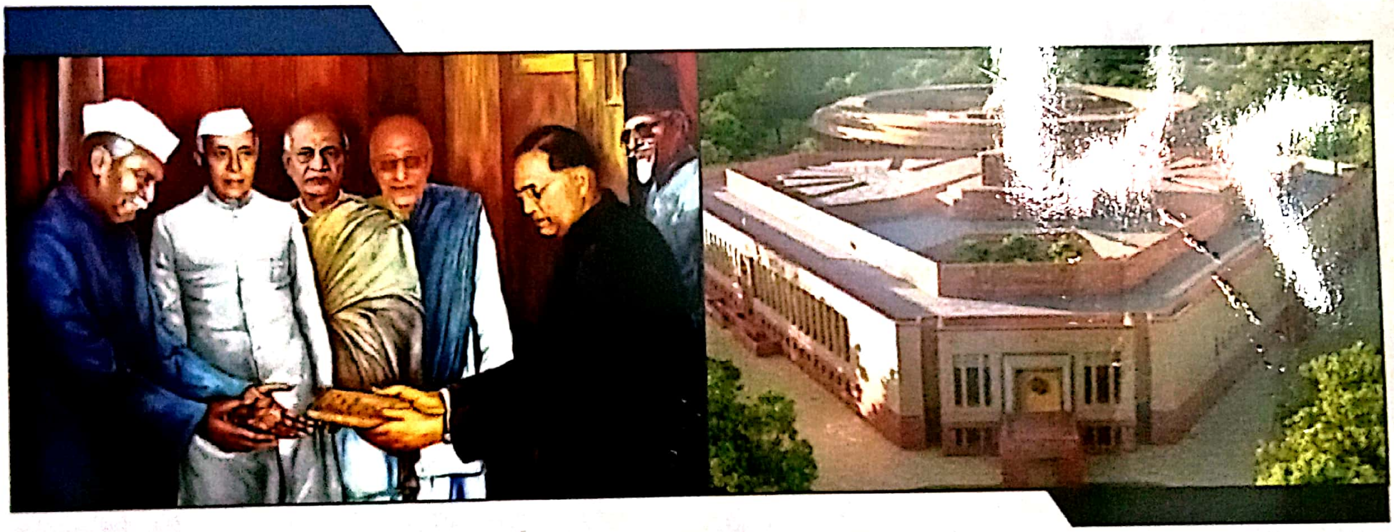

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42. सायबर गुन्ह्यांचे मानवी जीवनावर होणाऱ्या परिणामांचे अध्ययन 141
डॉ. प्रविण बाबुराव मोरे

43. भारतीय समाजासमोरील भ्रष्टाचार, धर्मभेद आणि भाषाविषयक समस्या : एक अभ्यास 143
डॉ.जयवंत पिराजी जुकरे

44. समान नागरी संहिताचे अवलोकन 148
प्रा. कांतिलाल गोवा वसावे, प्रा.डॉ. जयेश विक्रम पाडवी

45. भारतीय संविधान आणि समाजातील दुर्बल घटकांसाठी आर्थिक तरतूद : एक अभ्यास 150
प्रा. जीवन हटेसिंग सिसोदे

46. भारतीय संविधान : सामाजिक न्याय व लोकशाहीचे अध्ययन 152
प्रा. सुनिल मच्छिंद्रनाथ राजपूत

47. महाराष्ट्रातील आरक्षण धोरण : एक चिकित्सक अध्ययन 155
श्री. हर्ष अरुण नेतकर

48. दहशतवादाचे मानवी अधिकारावर होणाऱ्या परिणामांचे अध्ययन 157
करण लक्ष्मण थोरात

49. भारतातील भांडवलवाद, समाजवाद आणि लोकशाही : समकालीन चर्चेचे विश्लेषण 160
डॉ. नागेश खुशालराव गायकवाड

50. महिला सक्षमीकरणात कायद्याची भूमिका : एक अध्ययन 162
प्रा.डॉ. सुर्यवंशी मंगला सुरसिंग

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महिला सक्षमीकरणात कायद्याची भूमिका : एक अध्ययन

प्रा.डॉ. सुर्यवंशी मंगला सुरसिंग
शिक्षणशास्त्र विभाग प्रमुख, नानासाहेब य.ना. चव्हाण कला, विज्ञान व वाणिज्य महाविद्यालय, चाळीसगाव

प्रस्तावना :

प्राचीन काळापासून ते आधुनिक कालखंडापर्यंत भारताच्या सामाजिक व सांस्कृतिक इतिहासाचा मागोवा घेण्याचा प्रयत्न केल्यास त्यात स्त्रीयांना देण्यात आलेल्या दर्जाबाबत मोठी विभिन्नता आढळून येते. वैदीक काळात गार्गी, मैत्रयी, इंद्रायणी, घोषा, लोपमुद्रा मध्ययुगीन काळात रजिया सुलतान तर अर्वाचीन काळात सावित्रीबाई फुले, इंदिरा गांधी, किरण बेदी, प्रतिभाताई पाटील यासारख्या काही स्त्रीयांचा अपवाद वगळता अन्य कालखंडात मात्र पुरुषांच्या तुलनेत स्त्रियांना दुय्यम स्थान देऊन बहुअंशी त्यांचे मनुष्यत्व नाकारल्याचे दिसून येते. आज जगात सर्वत्र लोकशाही शासन व्यवस्था आहे. भारताने देखील लोकशाही शासन व्यवस्था स्वीकारुन सैध्दांतिक पातळीवर स्त्री–पुरुष समानतेचा स्वीकार केला आहे. तत्वत: आपणही भारतीय घटनेप्रमाणे लिंग भेदभाव अमान्य केला आहे. परंतु व्यवहार आणि वर्तनाच्या पातळीवर सर्वत्र लिंग भेदभाव धोरणाला पाठिंबा मिळत असल्याच्या पार्श्वभूमीवर आणि समता व समन्याय प्रस्थापनेच्या दृष्टीने स्त्री सक्षमीकरणासंदर्भात कायद्याची भूमिका महत्वपूर्ण ठरते.

महिला सक्षमीकरण संकल्पना :

स्वातंत्र्यपूर्व कालखंडात ब्रिटीश सरकारने स्त्रियासाठी केलेले सुधारणाविषयक कायदे व शिक्षण विषयक धोरणामुळे स्त्री सक्षमीकरणाला मोठी चालना मिळाली आहे. सतीप्रथा, बालविवाह, विधवा विवाह, केशवपन इ. अनिष्ठ प्रथा ायद्याने बंद झाल्या. १९ व्या शताच्या उत्तारार्धात स्त्री सबलीराची प्रीया ातीमान झाली. राजाराम मोहन रॉय, राजर्षी शाहू महाराज, महात्मा फुले, पंडिता रमाबाई आदि समाजसुधारांनी मनुवादी मानसितेला छेद देत महिला विषय सुधारणा कार्यात गतीमानता आणली. डॉ. बाबासाहेब आंबेडरांनी हिंदू कोड बिलाद्वारे स्त्रियांना कायदेविषयक हक्क, दर्जा आणि प्रतिष्ठेला गती मिळाली.

महिला सबलीरा ही संकल्पना व्यापक आहे. महिला सबलीकरण म्हणजे स्त्रियांचे अध्यात्मिक, राजनैतिक, सामाजिक किंवा आर्थिक सामर्थ्य वाढविणे. महिलांना सामाजिक, आर्थिक, शैक्षणिक, राजकीय, धार्मिक व प्रशासकीय क्षेत्रात समाविष्ट करुन त्यांचा सहभाग निर्णय प्रक्रियेत वाढवणे म्हणजे महिला सबलीकरण होय. महिला सबलीकरणात महिलांना अधिक सत्ता बहाल करणे, स्वत:च्या जीवावर स्वत:ची सत्ता प्रस्थापित करणे व पुरुषांची स्त्रियांच्या जीवनावरील सत्ता कमी करणे हे अभिप्रेत आहे. अबला महिलांना सबला करणे आणि त्यांना समान हक्क व संधी देणे. थोडक्यात स्वत्ववंचित व संधीवंचित महिलांना कोणत्याही भेदाशिवाय प्रातीक करण्याची संधी देणे म्हणजे महिला सबलीकरण होय.

स्त्री सबलीकरणाची गरज व महत्व :

१) **हक्काची जाणीव होयासाठी :** प्रत्येक स्त्रीला शिक्षण निवडीचा, स्वत:चे मत व्यक्त करण्याचा, संचार करण्याचा हक्क आहे. महिला संरक्षण कायदा १९९० महिलांच्या सर्वांगीण हक्काची जाणीव या कायद्याने होते. व याचे उल्लंघन कराणाऱ्यास दंडात्मक कारवाईची तरतूद नमूद केली आहे.

२) **स्त्री पुरुष समानता :** राज्यघटनेच्या प्रस्तावनेतच समान दर्जा व समान संधीचा उल्लेख आहे. घटनेतील कलम १४, १५, १६ मध्ये समानतेची तरतूद करण्यात आली आहे.

३) **स्त्रियांवर होणाऱ्या कौटुंबिक सामाजिक, लैंगिक अत्याचाराला वाचा फोडण्यासाठी :** कौटुंबिक हिंसाचार प्रतिबंधक कायदा २००५ या कायद्यातून सुनेला कायद्यात्मक संरक्षण प्रदान करुन महिला व बालकल्याण विभागामार्फत संरक्षण देण्याची तरतूद आहे.

४) **देशाच्या आर्थिक विकासास हातभार लावण्यासाठी :** महिलांना कलम ३९ (अ) प्रमाणे चरितार्थ चालविण्याच्या साधनांचा मूलभूत अधिकार आहे.

५) **पुरुषप्रधान संस्कृतीत स्त्रीविषयक दृष्टीकोन बदलण्यासाठी :** कलम ३९ (ड) प्रमाणे समान काम समान वेतन (१९५५) तर कलम ४२ नुसार महिलांना कामाच्या ठिकाणी पोषक वातावरण व सुविधा मिळाव्या म्हणून शासन कटीबध्द आहे.

स्त्री सबलीकरणातील अडथळे :

१) **पुरुषप्रधान संस्कृती :** स्त्री शिकल्याने अधिक सबल होईल व पुरुषांवर सत्ता गाजवेल या भितिने स्त्रियांना शिक्षण देण्यासाठी टाळले जाते. मुळात स्त्री अबला व दुर्बल नाही. स्त्रीला दुर्बल समजणे हे अधर्म व पाप आहे. असे महात्मा गांधी यंग इंडिया (एप्रिल १९३०) या पुस्तकात म्हणतात. स्त्री जवळ मोठी शक्ती आहे. तिला कमी लेखु नये म्हणून सरकारने महिला सबलीकरणासाठी राष्ट्रीय नियम २० मार्च २००१ मध्ये लागु केला.

२) **कौटुंबिक दारिद्र्य :** आर्थिक दारिद्र्यामुळे मुलाला शिवले जाते व मुलीच्या शिक्षणाकडे दुर्लक्ष केले

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❋ प्रकाशक ❋

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महाराष्ट्र राज्य साहित्य आणि संस्कृती मंडळाने या नियतकालिकेच्या प्रकाशनार्थ अनुदान दिले आहे. या नियतकालिकेतील लेखकांच्या विचारांशी मंडळ व शासन सहमत असेलच असे नाही.

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५४ Evaluating the Contribution of Small Finance Banks to Promote Financial Inclusion - Dr.Mahesh Abale, Prof.Rasika Dighde -------------------------- २६७

५५ Economic relations between India and Africa - 1) Dr.Jitendra Bagul, 2) Rupali Jaware, Akkalkuwa, Dist.Nandurbar ----- २७६

५६ To Study the role of digital technology transformation & it's growth towards education in India - Prof. Mayuresh Sangle ------------------------- २८०

५७ A Study of Literature and Society - Prof. Snehal Shinde, Aurangabad ------- २८४

५८ An analytical study on challenges faced by farmers to avail international agricultural financial trade of fresh grape export production with reference to Nashik District, Maharashtra - 1) Prof. Rohini Wakchaure, Nasik; 2) Dr.Ganesh Teltumbade, Nasik --------------------------------- २८९

५९ From Melancholic Depths to Euphoric Peaks: Analyzing Kamala Das's Emotional Landscape of Poetic World - 1) Prof.Shriya Mishra; 2) Dr. Monika Jaiswal, Moradabad, U.P. ------------------------- ३०१

६० The G20 Summit 2023: Gender Equality and Women Empowerment - 1) Smt.Monika Patel, Shahada, Nandurbar; 2) Dr.Arun Patil, Akkalkuwa, Nandurbar ---- ३०६

६१ Review Of Primary Health Care Centre In Pune District - Prof. Sangita Bharati, At Post Ale, Tal.Junnar, Dist. Pune ------------- ३१२

६२ Importance of National Education Policy-2020 In Imparting Education - 1) Dr. Rajendra More, 2) Dr. Sudhir kumar Srivastava, Taloda, Dist.Nandurbar ---------- ३१६

६३ Soft Skills in Personality Development - Dr.Mangala Suryawanshi, Chalisgaon, Dist.Jalgaon ----------------- ३२१

६४ A Spatial Analysis Of Road Transport Network Of Selected Sample Villages In Dhule District And Its Impact On Study Area: A Geospatial Analysis - 1) Dr.Chaitanya Nikam, 2) Dr.Manish Sawant, Nandurbar ------------ ३२४

६५ Privacy in the Digital Age: A Comprehensive Analysis of the Digital Personal Data Protection Act, 2023 - Prof.Twinkle Desai, Surat, Gujarat ----------- ३३०

६६ Impact of Intellectual Capital on Financial Performance of Indian Cement Industries - Dr.Tarit Kanti Sen, Bolpur, Burdwan ---------------------------- ३३५

६७ Reflection of Technological Dystopia in Ready Player One - 1) Yash Kandoi, 2) Dr.S.G.Chauhan ------------------------------ ३४४

६८ Vasudhaiva Kutumbakam in the context of G20 - 1) Dr. Sarika Patel, 2) Dr. Vinu Agrawal -------------------------- ३४६

६९ Review Of Primary Health Sub Center In Solapur District - Dr.Vahid Jamadar, Gunjoti, Tal.Omerga, Dist. Osmanabad ------------ ३५०

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Soft Skills in Personality Development

Dr. Prof. Suryawanshi Mangala Sursing
Head - Department of Education
Nanasaheb Y.N.Chavan Arts, Science & Commerce College,
Chalisgaon, Dist.Jalgaon

Abstract :

Today's education force the skill development. So central government and state government highly try beginning skill development. Our country formal skill training people is only 5% and other country UK - 68%, USA - 52% , Germany - 75% and South Korea - 96% so our country need skill development. Stand up India, Start up India, digital India concept program start. New Education Policy 2020 focus skill development, Central government established National skill development council (NSDC), Human Resource Development, University Grant Commission established community colleges. Kaushal (Knowledge up gradation skill Human Action and learning) scheme beginning. And made skill based human power and develop country. Human beings are need in more skills to develop personality and successful Achievement. skills are many types but mostly two types of skills.

1) Hard Skill
2) Soft Skill

If man is successful in his career life he need not only hard skill but also he need many soft skills, hard skills are related to the many subjects. For examples math, physics, zoology, botany, chemistry and both other hard skills are related in a mans Intelligence Quotient (IQ). But soft skills are related in mans Emotional Quotient (EQ).

Those skills can consist of social charms, conversation, talents, language skill, private conduct, Intellectual or emotional sympathy, leadership, time management, stress management, problem solving and decision making, Teamwork, communication, flexibility, patience, motivation, E-mail etiquette, etc. soft skill also known as 'People skills' or interpersonal skills. Soft skills relate to the way you relate to and Interact with other people.

Soft skills are character traits and Interpersonal skills that characterize a person's relationships with other people. In the workplace soft skills are considered a complement to hard skills, which refer to a person's knowledge and occupational skills. Sociologists may use the term soft skills to describe a person's "EQ" "Emotional Intelligence Quotient." As opposed to "IQ" "Intelligence Quotient".

If man wish successful profession he need Educational Ability. Advocate need LLB course, Doctors need MBBS, BAMS, Engineers need BE. He complete Educational Qualification and hard skill. But he wish successful career he need soft skills. So soft skill called subjective skill, people skills, Basic skills and Interpersonal skills.

• Meaning and Definition of Soft Skill :

1) Wikipedia defines soft skills as, "associated with person's 'EQ' (Emotional Intelligence Quotient), the cluster of personality traits, social graces, communications, language, personal habits, friendliness and optimism that characterize relationships with the other people."
2) Mind Tools defines soft skills as, "your work ethic, your attitude, your communication skills, your emotional intelligence and whole host of other personal attributes."

• Outstanding feature of soft skills :

1) "Soft skills are a cluster of productive personality traits that characterize one's relationship in a milieu. These skills can include social graces, communication abilities, language skills, personal habits, cognitive or emotional empathy, time management, teamwork and leadership traits."
2) Person life need soft skill are essential employment, career and successful.
3) Soft skill need person to make a Helping person become a key person in society. To socialize and help others everyone need soft skill.
4) Soft skill need person to communication in society.